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1976

PROJECT COMPLETION
REPORT NO. 487X

A SIMULATION MODEL OF TRITIUM KINETICS IN A FRESHWATER MARSH

By
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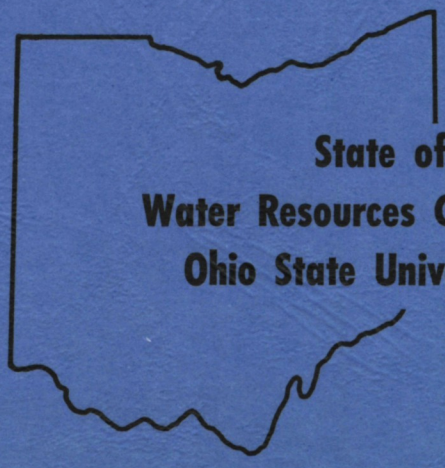
Ohio Cooperative Wildlife Research Unit
The Ohio State University

United States Department
of the Interior

CONTRACT NO.
A-038-OHIO



State of Ohio
Water Resources Center
Ohio State University

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This study was supported by the Office of Water Resources Research, U.S. Department of the Interior, Project A-038-OHIO. The research reported constituted the Ph.D. dissertation of Gary C. White.

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INTRODUCTION

The Atomic Energy Commission estimated that 120,000-170,000 megawatts of electricity (MWe) will be generated by nuclear reactors by the year 1980 (United States Atomic Energy Commission, 1967). The recent trend of electric power generating facilities toward the use of nuclear fission as an energy source undoubtedly will release increasing amounts of radionuclides into the environment.

Tritium (^{3}H), with a physical half-life of 12.35 years, is produced by nuclear reactors. Peterson et al. (1969) estimated that a 100-MWe pressurized water reactor (PWR) would release about 7,000 Curies of tritium per year into the environment. The projected release by the 872-MWe Davis-Besse Power Reactor is approximately 1,000 Curies per year into Lake Erie (United States Atomic Energy Commission, 1973). A weak beta emitter with a maximum energy of 18 kev, tritium is biologically important because it substitutes for protium (^{1}H).

Jacobs (1968:75) estimated the natural annual production of tritium to be about 4 to 8 megacuries. This results in a steady state tritium inventory of 70 to 140 megacuries. On the basis of these projections and the projected increase in fission-product tritium production, the rate of production of fission-product tritium will exceed that of natural tritium by the year 1990 (Jacobs, 1968).

As a result of this significant increase in tritium production, it becomes important to better understand the kinetics of tritium in

environment. Relatively little study has been made of the cycling of tritium through the biotic and abiotic compartments of natural ecosystems. Elwood (1971) pointed to the lack of information concerning tritium kinetics in temperate climates and aquatic food chains. Although little concentration of tritium by aquatic organisms has been shown, the increased quantities of tritium released to the natural environment suggest that further knowledge of tritium kinetics is desirable. Hatch and Mazrimas (1972) demonstrated the incorporation of tritium from tritiated water into the DNA of laboratory mice. There is an unresolved question of whether the incorporation of tritium into the macromolecules imparts any special hazard to the organism due to the unique properties of tritium radiation, or the isotope's transmutation into a positively charged helium nucleus upon decay (Hatch and Mazrimas, 1972).

Modeling the flow of tritium through a marsh ecosystem provides a valuable quantitative description of the radionuclide's interactions with the environment. The mathematical equations provide a useful shorthand for describing the complex movements of tritium throughout the food web.

Modeling is of value both during the model's developmental stages and after the model is completed. When the investigator is initially developing the block diagrams for the model, he is forced to rigorously clarify his idea of the system's structure, and the block diagram represents a hypothesis concerning this structure. Also additional information, such as which parameters are required, is emphasized by the block diagram. The completed model provides a very useful

predictive tool. The model is assumed to provide a realistic simulation of the system. The tritium model developed in this study will be of value in predicting the loss of tritium from a marsh contaminated from an accidental spill or the uptake of tritium by the marsh from a contaminated atmosphere.

Few investigators have constructed realistic models of tritium kinetics in the environment. Stewart et al. (1971) studied the discrimination and concentration of tritium in freshwater microcosms. They presented considerable data on tritium kinetics in the microcosms, but did not consider the influence of environmental variation. Their modeling efforts consisted of fitting sums of exponentials to the observed data for the compartments sampled. They did not mathematically model the exchange of tritium between the organism body water and tissue compartments. Many investigators have studied the uptake and loss of tritium within a single species, including Patzer et al. (1973), Adams and Peterle (1975), Rosenthal and Stewart (1971), and Harrison and Quinn (1972). However, no studies have been done that consider the effect of environmental variables on such data so that the results can be extrapolated to whole natural ecosystems.

Horton et al. (1971) developed a model to explain the loss of tritium from an impermeable basin. However, they did not extend their model to permeable basins. Neither did they incorporate environmental data in estimating model parameters. Furthermore, few investigators have looked at tritium kinetics on a whole system basis. Lehman (1973a, b) studied the loss of tritium from a Lake Erie marsh but suggested only a very simple model of tritium loss from the

marsh water. Jordon et al. (1974) studied the movement of tritium through soil and compared the observed data with a mathematical model they developed, but parameter estimates were not obtained from the field data.

Parameter estimates for models of tritium kinetics have not been developed from data observed in natural ecosystems. Bloom and Raines (1970) described a whole system model of tritium kinetics in a tropical forest system, but parameter estimates were obtained from simple laboratory experiments, or were approximated to provide for realistic model performance. Other contaminants, however, have been modeled with data collected from natural systems. Eberhardt et al. (1971) developed a model of DDT kinetics in a Lake Erie marsh. A compartmental model was assumed and parameters were estimated from the observed data with nonlinear least squares. Forsyth et al. (1974) performed the same type of analysis of DDT kinetics in an old field system. In these modeling efforts, compartment models were assumed, based on knowledge of DDT kinetics, and the parameters of the model were estimated from the observed data.

Parameters estimated from data observed in a real ecosystem reflect the variation in environmental conditions that are reality, hence correspond more closely to actual environmental conditions, not to the controlled environment of laboratory experiments. Ecologists are not yet to the level of knowledge that heuristic models based on "first principles" have good predictive value. Too little is understood about the interactions of ecosystem components. The risk that an incorrect model can be made to fit the observed data is high, however, and the

appropriateness of the assumed model is critical to the validity of the parameter estimates. If the assumed model is a good representation of the process, then the parameters estimated should be realistic and the model is therefore a good approximation of the real system. The knowledge of tritium kinetics has advanced to the point that a realistic model of tritium kinetics can be assumed, and the parameters can be estimated from real ecosystem data.

Parameter estimation from ecosystem tracer studies is somewhat more complicated than for physiological tracer studies. Ecosystem tracer studies tend to be measured in weeks or months rather than hours or days and exhibit more variability due to environmental variability. The simplest assumption about the randomness in the data is to assume that all errors are due to sampling error, that is, the process cannot be observed exactly and so the process plus some random error is observed. Parameters typically are estimated by minimizing the sum of squared errors, or the least squares method. If the random error can be assumed normally distributed with mean zero and some constant and finite variance σ^2, and if all the errors can be assumed independent and identically distributed, then the parameter estimates obtained by the least squares method are also maximum likelihood estimates. A maximum likelihood estimator has some known and desirable properties, namely that the estimators are consistent and asymptotically efficient. Stated more simply, estimates from large samples are unbiased, although estimates from a small sample may be biased. As the sample size approaches infinity, the variance of the estimate approaches zero. Eberhardt et al.

(1971) and Forsyth et al. (1974) developed parameter estimates for models of DDT kinetics based on these assumptions.

However, assumptions made above concerning the errors in the data can be questioned for the type of data to be used in this study. The procedure implies that the observed process is deterministic, and that there is no randomness in the process. This is an unrealistic assumption, as an ecologist will recognize, since randomness is expected in the real world. Fluctuations in temperature and rainfall, e.g., show stochastic properties. Hence the true process does not behave exactly as expected but fluctuates randomly about the expected level due to the stochastic properties of the environment. In this study, the loss of HTO from the marsh will be one of the observed processes. Because of the random environmental fluctuations, the rates of loss of HTO from the marsh would be expected to fluctuate randomly. The assumption of all sampling error does not allow for this sort of fluctuation. Because the assumption may be false, the parameter estimates obtained from maximum likelihood theory may be wrong.

Some study has been made of the problem. Matis and Hartley (1971) described a method for estimating compartment parameters from time series data when the movement of material between compartments is assumed to be a stochastic process. Their method assumes, however, that compartment volumes are known, which is seldom true for ecosystem tracer studies. Moreover, their model does not allow for an error of observation. Eberhardt and Nakatani (1969) suggested that the parameters in compartment models should be considered random variables. Solutions to differential equations in which the parameters are random variables are

very difficult and will not be attempted. However, a method of estimating the parameters, in which both process and sampling variation are assumed, will be shown. This method allows fewer assumptions concerning the randomness in the model.

The objectives of this study were to (1) develop a model of tritium kinetics in a marsh system from data observed in a natural system under environmental variation, (2) demonstrate the utility of the model in predicting tritium kinetics in the marsh system, and (3) develop maximum likelihood estimators of model parameters that assume both sampling and process variation.

STUDY AREA AND DATA COLLECTION PROCEDURES

Study Area

The study unit, a 2-ha enclosed area of Navarre Marsh, was located in northwestern Ohio, approximately 32 km east of Toledo. Physical and chemical parameters of the marsh were reported by Lehman (1973a). Briefly, the unit contained about 10,000 m^3 of water at a mean depth of 50 cm. The upper 30 cm of sediment was largely organic matter. A clay stratum was present below this depth. Twenty-six species of macrophytes inhabited the area. The predominant ones were coontail *(Ceratophyllum demersum)*, water milfoil *(Myriophyllum exalbescens)*, yellow water lily *(Nuphar advena)*, smartweed *(Polygonum* sp.*)*, pickerelweed *(Pontederia cordata)*, pondweed *(Potamogeton* sp.*)*, and arrowhead *(Sagittaria latifolia)*. A variety of vertebrate and invertebrate fauna was present, including bluegills *(Lepomis macrochirus)*, carp *(Cyprinus carpio)*, crayfish *(Procambarus blandingi)*, and bullheads *(Ictalurus melas* and *I. natalis)*.

Adams et al. (1975) applied approximately 11 Curies (Ci) of tritium (as tritiated water, HTO) to the study area on 29 October 1973. Prior to tritium application, depth of the study area was reduced from 50 to 35 cm with a diesel powered, 25.4-cm centrifugal pump. On the date of application, water was pumped into the study area from an adjacent marsh unit and the tritiated water (1,000 ml) added to the effluent through a chemical feed pump. The water was discharged at the center of the study area, and tritium was fairly uniformly

distributed throughout the marsh water (0.00112 μCi/ml) by the third day following application.

Lehman (1973a, b) treated the study area with 1.3 Ci of HTO on 10 July 1972. HTO concentrations in the marsh water were observed for 152 days. Lehman's methods of application were identical to those described above.

Sampling Procedures

Samples (20 ml) of marsh water were taken daily during the first week following tritium application (Adams et al., 1975). Weekly samples were taken through March, 1974, after which monthly samples were taken. Samples of marsh water were taken from at least seven locations in the marsh for each sampling period. Samples were transferred to the laboratory in air-tight bottles, where the sample was filtered before they were counted for tritium activity.

Levels of HTO in the atmosphere were taken from measurements of tritium activity in water vapor. Water vapor was collected from an aluminum pipe with the lower end placed in a vacuum bottle of liquid nitrogen. The pipe was cooled by the nitrogen, and water vapor condensed on the pipe. When all the nitrogen evaporated, the pipe warmed and the condensed vapor thawed and flowed into the vacuum bottle. This water was counted for tritium activity. While the water vapor was being collected, relative humidity and temperature were also measured with a wet and dry bulb thermometer.

Daily sediment samples were taken with a gravity-stratification corer (Wildlife Supply Company, Saginaw, Michigan 48602) during the

first week following tritium application (Adams et al., 1975). Four sediment cores then were collected on a weekly basis through March 1974, after which monthly samples were taken. Samples were transferred to the laboratory in air-tight containers and frozen. One-cm layers were taken from individual cores at 5-cm increments to a 20-cm depth.

Three days following application, a 76.2-cm square enclosure (wood frame and hardware cloth) containing crayfish *(Procambarus blandingi)* (average individual weight was 28.3 g) was placed in the study area from an adjacent uncontaminated marsh unit. Samples were taken from this enclosure 0.5, 1, 2, 3, and 5 hours following placement in the area. Daily samples then were taken during the first week, followed by weekly sampling through March 1974. After this date, biweekly samples were collected. Immediately following collection, organisms sampled were placed in plastic bags, frozen in liquid nitrogen, and transported to the laboratory where they were kept frozen until analyzed.

Sample Preparation

The tritiated water recovery system described by Stewart et al. (1972) was used for tissue sample preparation. The sample was vacuum freeze dried to remove tritiated water (unbound tritium) from the tissue. This water was then counted for tritium activity with a Model 3320 Automatic Tri-Carb® Liquid Scintillation Spectrometer (Packard Instrument Co., Downers Grove, Illinois 60515). The dried tissue was oxidized (Model 300 Packard Instrument Co.) to remove the remaining tritium in the sample (bound tritium) in the form of HTO, which was

then counted for tritium activity. Tritium activity was not corrected for physical decay since this was not significant for the time period considered.

The freeze drying method of tissue sample preparation produces different unbound to bound tritium concentration ratios than the method used by Lehman (1973a) (Adams, personal communication). In Lehman's method, following that of Hatch and Mazrimas (1972), the sample was dried in the oxidizer before combustion. Hence tissue data from Lehman (1973a) were not incorporated into the model. The freeze drying method is the method more frequently mentioned in the literature and appears to provide the more consistent method of separating unbound and bound tritium from tissue samples. Therefore, parameter estimates for the model should be estimated with data from freeze-dried tissue so that the model is compatible with the majority of the reported work.

The data used in this study were collected as part of the Ph.D. work of Lowell W. Adams, The Ohio State University. The actual data values and an in-depth description of the collection and preparation procedures will be presented by him in his dissertation.

WATER SEDIMENT MODEL I

Models of radionuclide kinetics traditionally have been conceptualized as compartmental models. The flow from a compartment is assumed to be proportional to the quantity of material contained in the compartment. A single compartment was assumed to describe the HTO concentration in the initial attempt to model HTO kinetics in the marsh water. If the loss rate of HTO from the marsh water is always assumed to be proportional to the HTO concentration in the marsh water, the simple differential equation is formed:

$$\frac{dW_c}{dt} = -\lambda W_c$$

The solution is

$$W_c(t) = W_c(0) \exp(-\lambda t) \qquad (1)$$

where $W_c(t)$ is the actual HTO concentration in the marsh water at time t, and λ is the loss rate coefficient (day^{-1}). The observed HTO concentration, i.e., $W_c^*(t_i)$, in the marsh water was assumed to contain an additive sampling error, normally distributed with mean zero and variance σ^2, independent and identically distributed for each observation. The variance of the sampling error may be proportional to the magnitude of the true concentration, hence a multiplicative process error should be used. A multiplicative error was not assumed, however. The additive error model used to fit equation (1) was:

$$W_c^*(t_i) = W_c(0) \exp(-\lambda t_i) + e_i$$

where e_i is the associated sampling error for sample i taken at time t_i. The nonlinear least squares computer routine developed by Marquardt (1963) was used to estimate $W_c(0)$ and λ. Partial derivatives of $W_c(t_i)$ with respect to each parameter are required by the least squares algorithm and were calculated analytically, i.e.

$$\frac{\partial W_c(t)}{\partial W_c(0)} = \exp(-\lambda t), \text{ and } \frac{\partial W_{c(t)}}{\partial \lambda} = W_c(0)(-t)(\exp(-\lambda t)).$$

Estimated values for the parameters were $W_c(0) = 2512$ dpm ml^{-1} and $\lambda = 0.010737$ day^{-1} (asymptotic standard errors were 39.13, and 0.00042, respectively, Dixon [1970]).

This equation then was used as input to the sediment model. Ninety-two percent of all tritium in the sediment was present as HTO, so the remaining 8 percent adsorbed to sediment particles or organic matter was ignored to simplify the model. Inspection of the data suggested that a simple diffusion model might adequately predict tritium concentrations as a function of time and depth into the sediment. The simplest partial differential equation describing the process was (Crank, 1975):

$$\frac{\partial S}{\partial t} = \frac{D\partial^2 S_c}{\partial x^2}$$

where S_c is the diffusible tritium concentration in the sediment (dpm ml^{-1} H_2O), x is the depth into the sediment (cm), t is the time since tritium application to the marsh (day), and D is the

diffusion constant ($cm^2\ day^{-1}$). The equation was solved given the following initial and boundary conditions (White, 1976:96-98):

Condition 1: $S_c = 0$ at $t=0$ and $x > 0$,

Condition 2: $S_c = W_c(0) \exp(-\lambda t)$ at $t \geq 0$ and $x=0$, and

Condition 3: $\frac{\partial S_c}{\partial t} = 0$ at $t \geq 0$ and $x=L$,

where λ is the loss rate coefficient of tritium from the marsh water, $W_c(0)$ is the tritium concentration of the marsh water at $t=0$, and L is the depth (cm) into the sediment to which tritium diffuses.

The second condition on the function S_c implied the surface of the sediment was the same tritium concentration as the overlying water. The third condition implied that tritium diffused into the sediment to a depth L, which was set at approximately 30 cm because a relatively impermeable clay layer occurred at that point. No tritium was assumed to diffuse beyond 30 cm. The solution, derived in White (1976: 96-98) is:

$$S_c = \frac{W_c(0) \exp(-\lambda t) \cos(\sqrt{\lambda/D}\,(L-x))}{\cos(\sqrt{\lambda/D}\,L)}$$

$$-W_c(0) \sum_{n=1}^{\infty} \frac{\exp\left\{\frac{-(2n-1)^2 \pi^2 Dt}{4L^2}\right\}}{(-1)^n \left\{\frac{L^2}{(2n-1)\pi D} - \frac{(2n-1)\pi}{4}\right\}}$$

$$\cdot \cos\left\{\frac{(2n-1)\pi(L-x)}{2L}\right\} \qquad (2)$$

This equation was fitted to the concentration of tritium in the sediment water (unbound tritium) by nonlinear least squares. $S_{c_i}^*$ is defined as the i^{th} sample mean of 2-4 data points. Then $S_{c_i}^* = S_c + \varepsilon_i$, where the ε_i was assumed to be additive and normally distributed, with mean zero and constant variance. The previously estimated values of $W_c(0)$ and λ were used. The partial derivative of the function S_c with respect to D was calculated numerically (White, 1976:92-95). Data (2-4 samples) were taken at depths of 1, 5, 10, 15 and 20 cm, providing 5 values of $S_{c_i}^*$. The value of D was approximately 0.52 $cm^2\ day^{-1}$ (asymptotic standard error 0.0273, Dixon [1970]). Plots of equations (1) and (2) and the observed data are presented in Figs. 1-6.

The water-sediment data in Figs. 1-6 were collected over a wide range of naturally varying environmental conditions (October 1973 to September 1974). The simple models fit the observed data better than might be expected. However variation in HTO kinetics due to environmental variation probably was incorporated into the parameter estimates for λ and D, so that models of this sort may have poor predictive value for other time periods or study areas.

The water loss rate coefficient (λ) can be compared to values for other studies. Horton et al. (1971) showed that λ is a function of the depth of the water. They assumed that HTO evaporates independently of H_2O, since evaporation of water into the atmosphere is usually limited by the diffusion of water vapor through a quiescent layer of air near the surface. H_2O and HTO will diffuse through the quiescent layer to

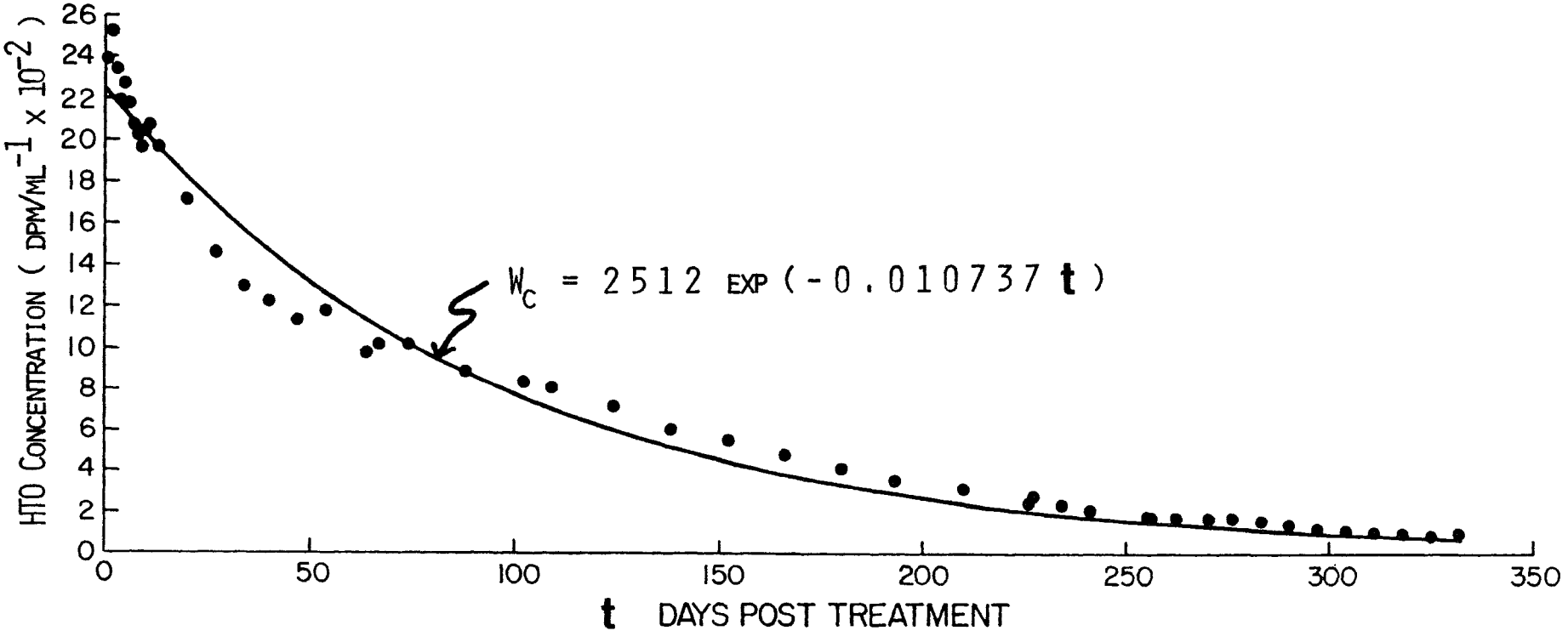

Fig. 1. Loss of tritium from the Navarre Marsh water, 1974. The solid line represents a single exponential function fit to the data for water sediment model I.

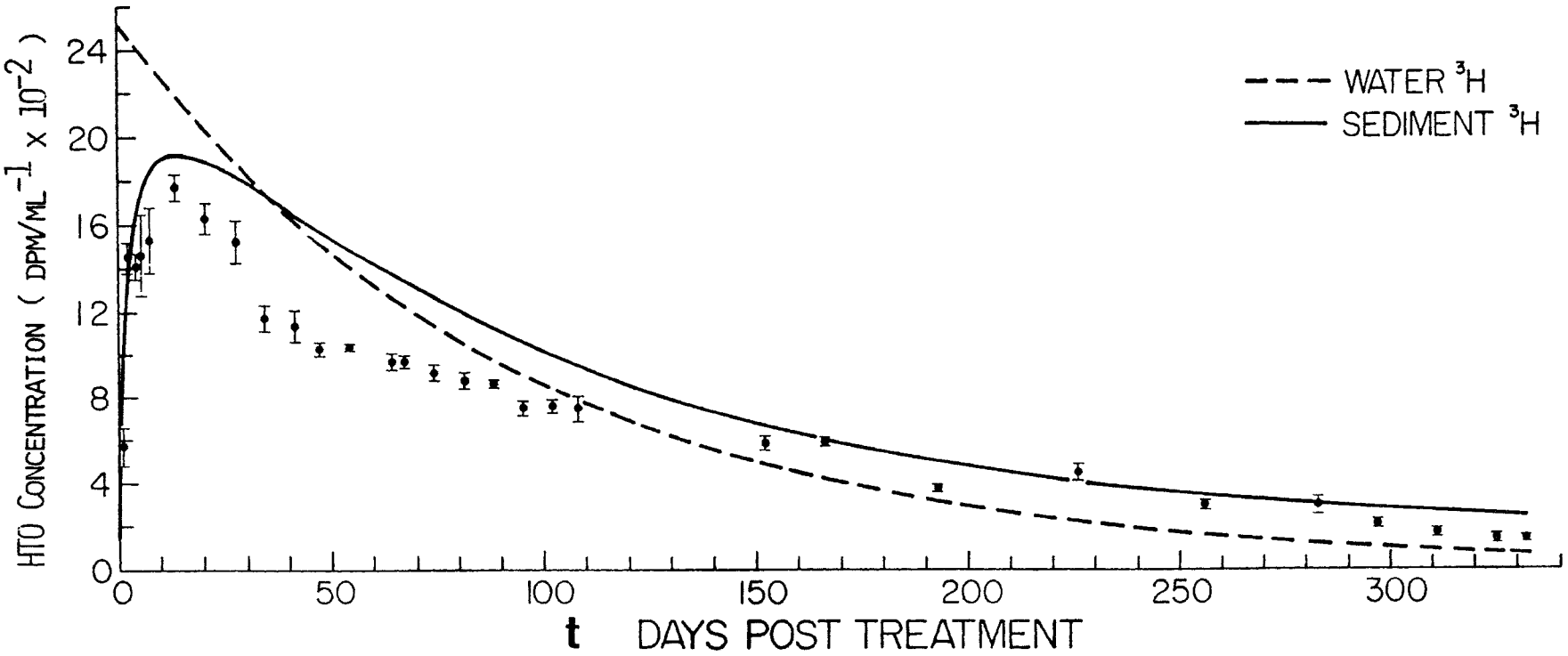

Fig. 2. Uptake and loss of tritium in the top 1-cm sediment layer. The solid line is the predicted sediment concentration and the dashed line is the predicted water concentration by water-sediment model I. Data points represent the means of 2-4 samples ± 1 standard error.

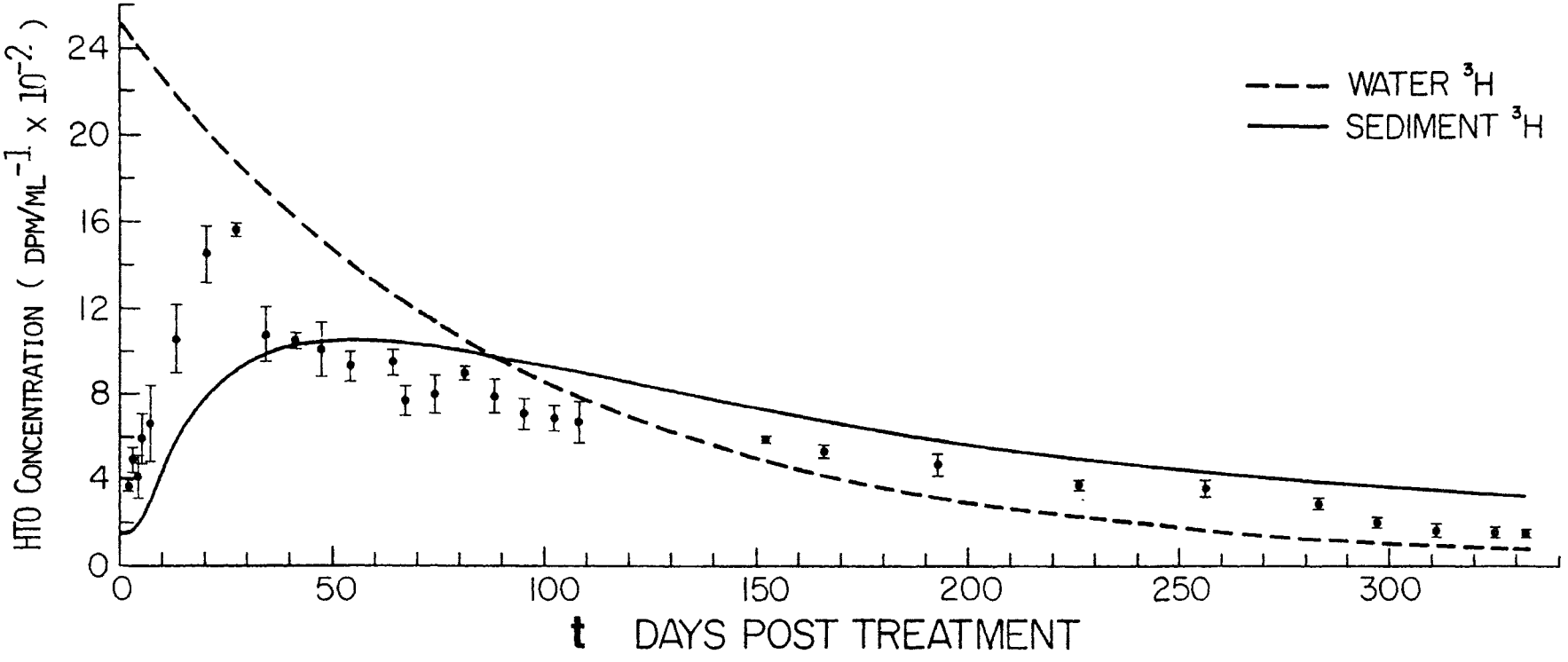

Fig. 3. Uptake and loss of tritium in the 5-cm sediment layer. The solid line is the predicted sediment concentration and the dashed line is the predicted water concentration by water sediment model I. Data points represent the means of 2-4 samples ± 1 standard error.

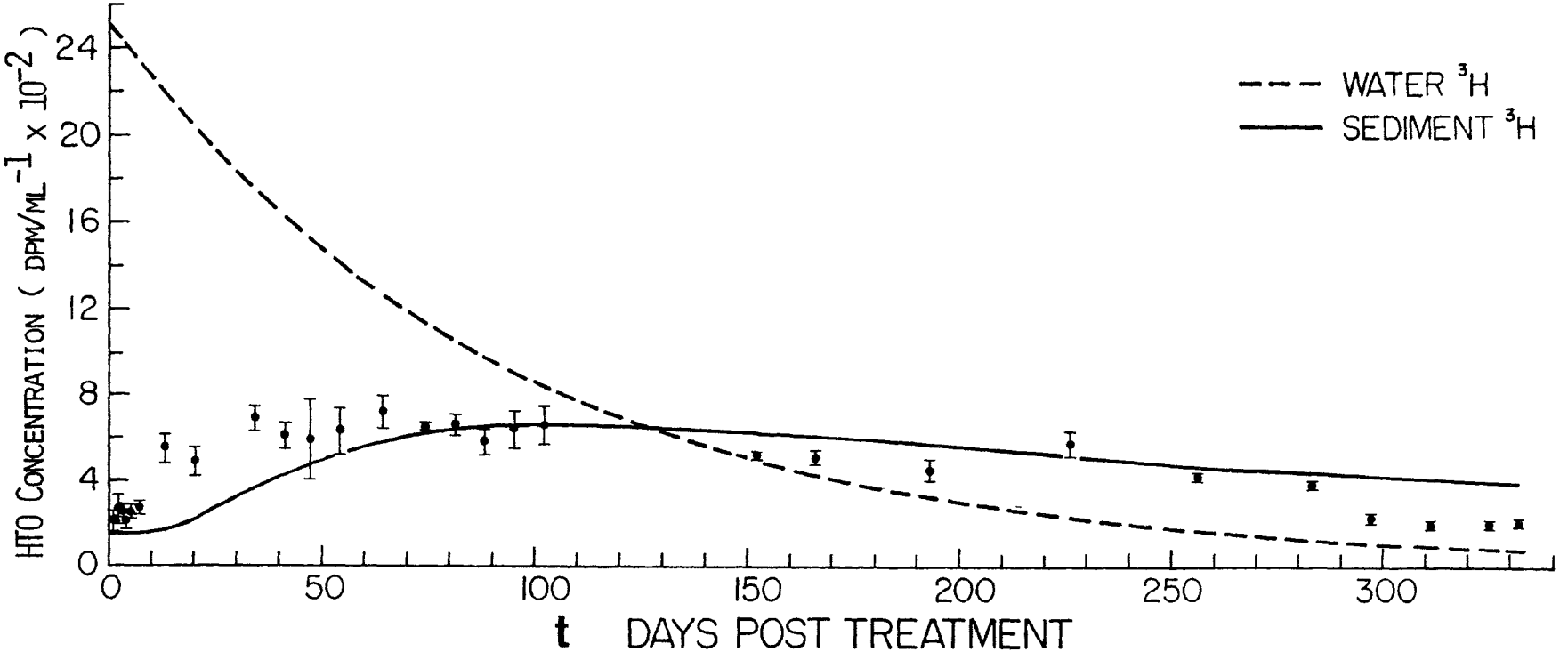

Fig. 4. Uptake and loss of tritium in the 10-cm sediment layer. The solid line is the predicted sediment concentration and the dashed line is the predicted water concentration by water-sediment model I. Data points represent the means of 2-4 samples ± 1 standard error.

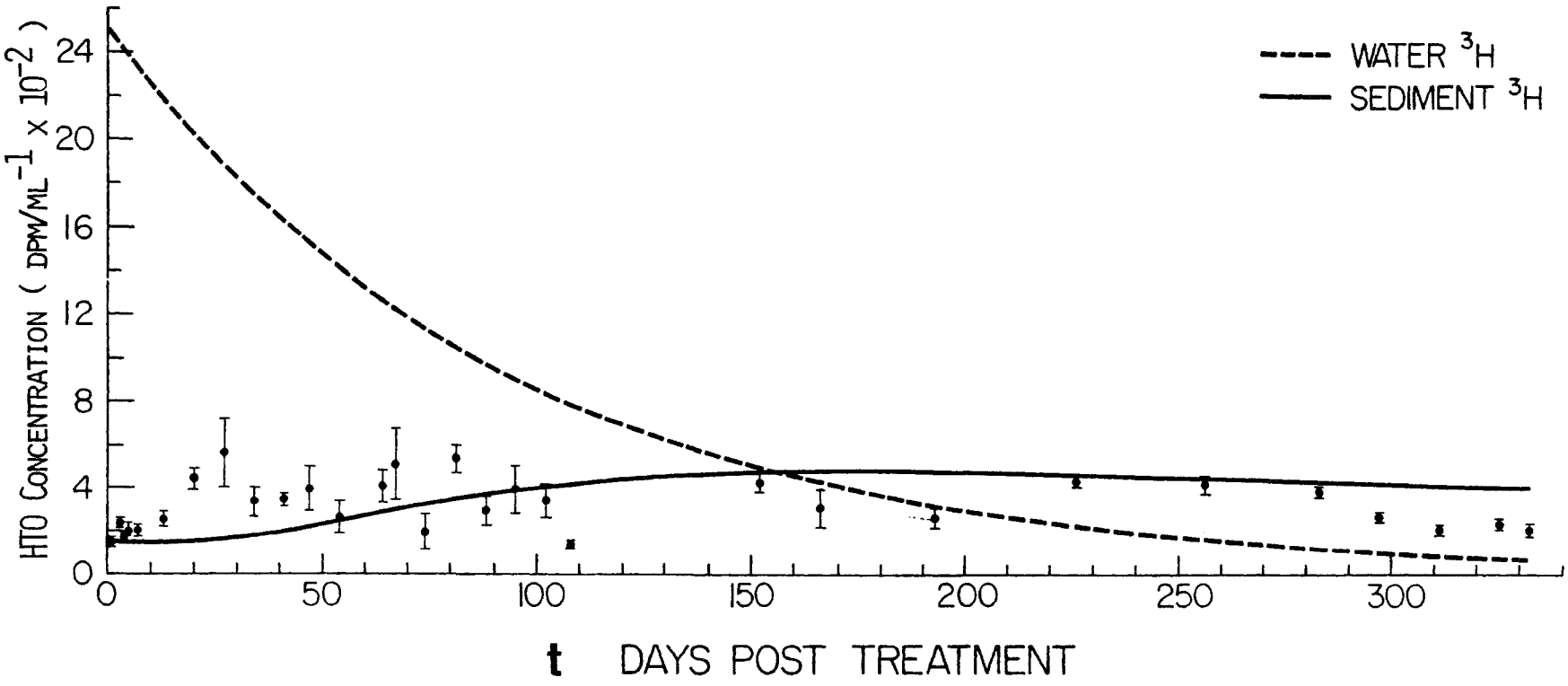

Fig. 5. Uptake and loss of tritium in the 15-cm sediment layer. The solid line is the predicted sediment concentration and the dashed line is the predicted water concentration by water-sediment model I. Data points represent the means of 2-4 samples ± 1 standard error.

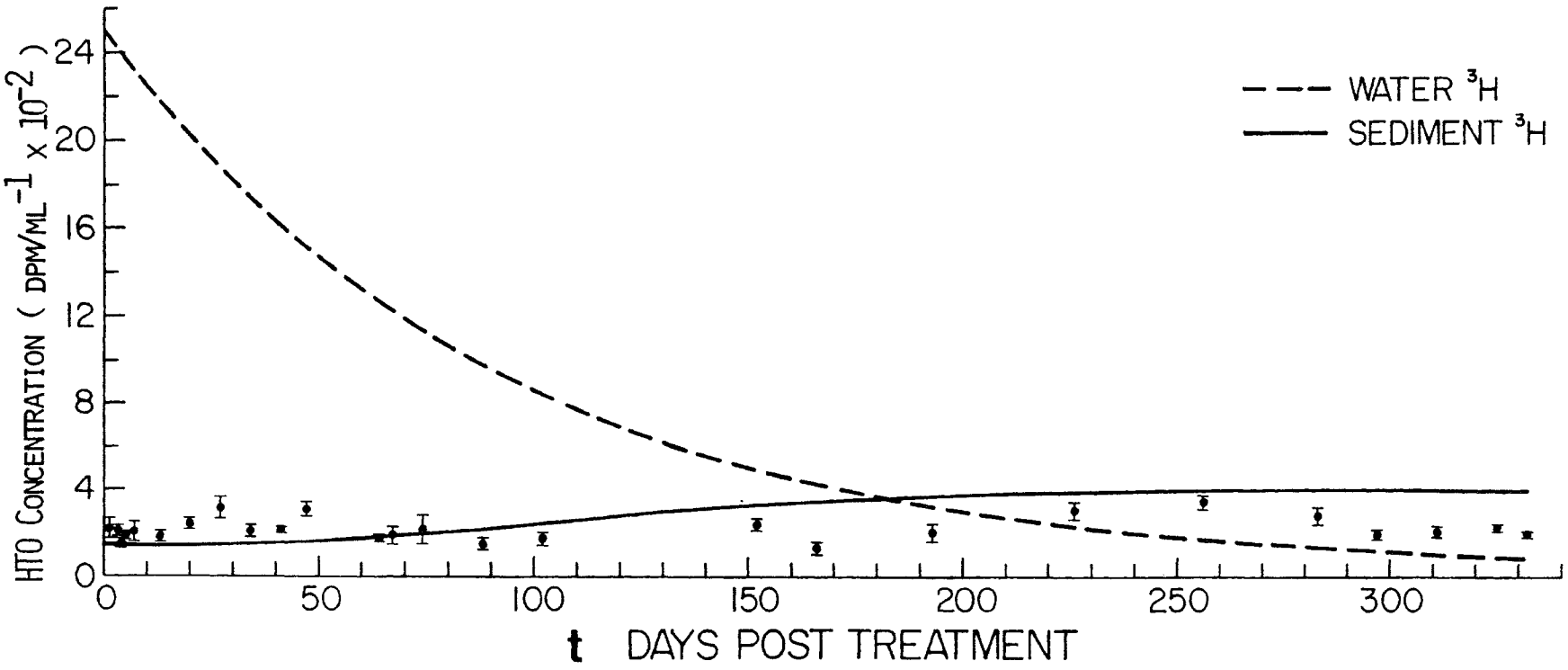

Fig. 6. Uptake and loss of tritium in the 20-cm sediment layer. The solid line is the predicted sediment concentration and the dashed line is the predicted water concentration by water-sediment model I. Data points represent the means of 2-4 samples ± 1 standard error.

a first approximation as if the other were not present, because the partial pressure of each is small compared to that of air. In their notation $\lambda = \beta/z_0$, where β is constant for constant environmental conditions and z_0 is the water depth (cm). For the value estimated in my study, $\beta = 0.537$ cm day^{-1}. Horton et al. (1971) found $\beta = 0.552$ cm day^{-1} for an impermeable basin 410 cm deep in Georgia. Lehman (1973b) found a loss rate coefficient of $\lambda = 0.017$ day^{-1} for the Navarre Marsh unit during the summer and fall of 1972. Multiplying by depth gives $\beta = 0.85$ cm day^{-1}. Because β is a function of environmental conditions, a wide range of values could be expected. Environmental parameters affecting β were utilized to improve the water-sediment model.

WATER SEDIMENT MODEL II

Model Development

In the previous attempt at modeling the flow of HTO in the marsh water and sediment, the two compartments were assumed not connected by direct flows. This was a poor assumption, because 20 days after application the sediment contained 1.2 Ci of the 11 Ci of tritium applied to the marsh. Hence a significant flow of tritium occurred from the marsh water into the sediment, and eventually back again. Therefore, the water-sediment model was reformulated into a 31-compartment model. The sediment was represented by 30 compartments, each a 1-cm layer, since at the 30-cm depth an impermeable clay layer was present. The system is presented diagramatically in Fig. 7.

Transfers between compartments were assumed proportional to the concentration gradient between compartments, which is equivalent to a donor controlled system with the same transfer coefficient between two compartments. For the water compartment, W, flows were to the atmosphere and to the first sediment layer, S_1. For the first sediment layer, S_1, flows were to the water and to the second sediment layer. The rate of change in concentration for the first sediment layer is

$$\frac{dS_{c1}}{dt} = D\ (W_c - S_{c1}) - D\ (S_{c1} - S_{c2}) \qquad (3)$$

where W_c is the water HTO concentration in dpm cm^{-3}, S_{ci} is the sediment HTO concentration in the i^{th} layer in dpm cm^{-3}, and D is

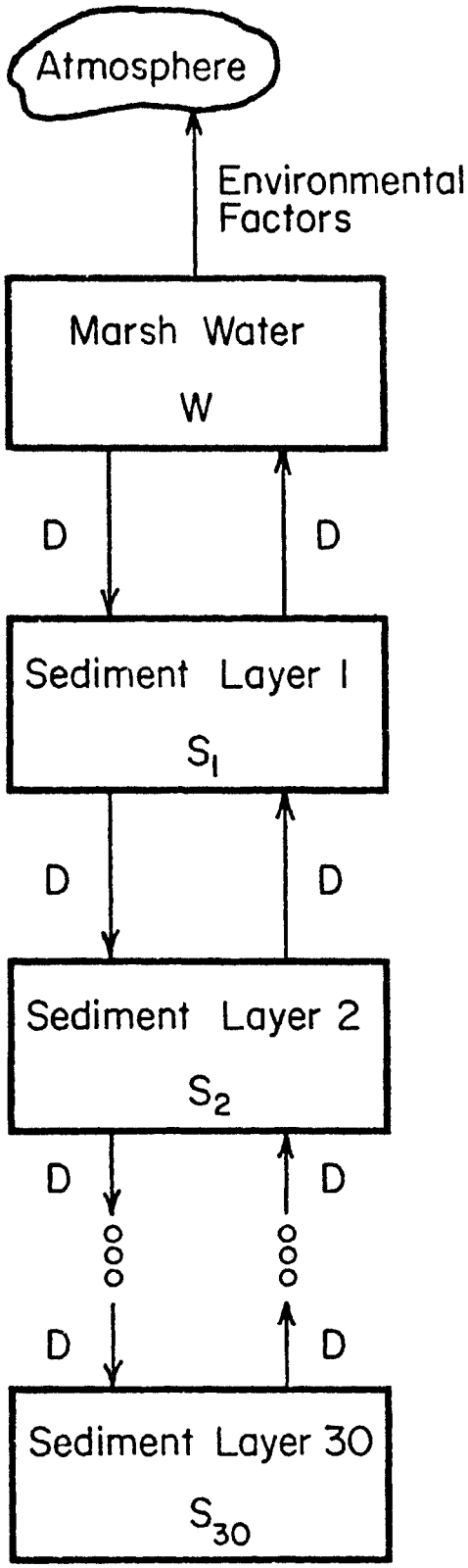

Fig. 7. Thirty-one compartment model of HTO kinetics in the marsh water and sediment.

the transfer constant in day^{-1}. The net flow rate of HTO to the first sediment layer from the water is equal to the rate of change of S_{c1} due to W_c times the volume of S_1, or

$$F_s = D\ (W_c - S_{c1})\ V_{s1} \tag{4}$$

where V_{s1} is the volume of the first sediment layer in cm^3 and F_s is the flow rate in dpm day^{-1}.

The loss of HTO to the atmosphere usually is limited by the diffusion of water vapor through a quiescent layer of air near the surface according to Horton et al. (1971). They presented a model describing the loss of HTO to the atmosphere, which was modified to provide for the different concentration units, thus

$$F_a = Ak'(P_T - P_T^0\ k''W_c M_w/\rho) \tag{5}$$

where F_a is the rate of HTO loss to the atmosphere in dpm day^{-1}, P_T is the partial pressure of tritium in the atmosphere in g cm^{-1} day^{-2}, P_T^0 is the equilibrium vapor pressure of HTO concentration of water in g cm^{-1} day^{-2}, W_c is the HTO concentration of water in dpm cm^{-3}, M_w is the molecular weight of H_2O, g $mmol^{-1}$, ρ is the density of H_2O, g cm^{-3}, k'' is the conversion from dpm of HTO to mmol of HTO, 1.548×10^{-14} mmol dpm^{-1}, k' is the proportionality constant, dpm day g^{-1} cm^{-1}, and A is the surface area of the marsh, cm^2. The loss of HTO from the marsh water can be described by combining equations (4) and (5):

$$\frac{dW_m}{dt} = -F_s + F_a = -D\ (W_c - S_{c1})\ V_{s1} + k'A(P_T - P_T^0\ k''W_c M_w/\rho) \tag{6}$$

where W_m is the amount (mass) of HTO in the marsh water in dpm. The concentration of HTO in the marsh is related to mass of HTO as

$$W_m = W_c V_w \tag{7}$$

where V_w is the volume of marsh water. V_w is equivalent to the marsh area times the marsh depth so that $V_w = A\ z_w$. Marsh depth is a function of time, since the marsh depth changes from evaporation and rainfall. Substituting ($A\ z_w$) for V_w into equation (7) and differentiating with respect to time gives:

$$\frac{dW_m}{dt} = \frac{dW_c}{dt}\ A\ z_w + \frac{dz_w}{dt}\ A\ W_c \tag{8}$$

Setting equation (8) equal to equation (6) and simplifying leads to an expression for the change in HTO concentration in the marsh water:

$$\frac{dW_c}{dt} = \frac{1}{z_w}\ \{-W_c\ (\frac{k'\ P_T^0\ k''M_w}{\rho} + \frac{d\ z_w}{dt})\ -\ z_{s1}\ D(W_c - S_{c1})\ +\ k'P_T\} \tag{9}$$

where z_{s1} is the depth of the first sediment compartment (1 cm), and $z_{s1} = V_{s1}/A$.

The equation for the sediment compartments is equivalent to equation (3), so the following set of equations is used to describe the kinetics of HTO in the upper 30 cm of sediment:

$$\frac{dS_{c1}}{dt} = D\ (W_c - S_{c1}) - D\ (S_{c1} - S_{c2})$$

$$\frac{dS_{c2}}{dt} = D\ (S_{c1} - S_{c2}) - D\ (S_{c2} - S_{c3})$$

$$\vdots \qquad (10)$$

$$\frac{dS_{c29}}{dt} = D\ (S_{c28} - S_{c29}) - D\ (S_{c29} - S_{c30})$$

$$\frac{dS_{c30}}{dt} = D\ (S_{c29} - S_{c30})$$

Expressions were required for the marsh water depth z_w, equilibrium vapor pressure P_T^0, and partial pressure P_T to estimate the parameters of the above equations from the observed marsh water and sediment data. A function for z_w was found by fitting observed depth data to a fourth degree polynomial with time as the independent variable and additive errors. The polynomial coefficients in order of increasing powers of time were 49.213, -0.11364, 6.7696E-3, -3.5977E-5, and 4.8347E-8. This polynomial provided a good fit to the observed data. An alternative approach would involve the equation given by Horton et al. (1971) to describe changes in depth, with inputs of evaporation rate and rainfall. However, for the purposes of estimating the parameters affecting HTO loss, the empirical method used seemed to best meet the objectives of the study.

A function for P_T^0 was developed from data presented by Sepall and Mason (1960). They provided the ratio of equilibrium vapor pressures for H_2O to HTO at various temperatures. The vapor pressure for HTO was

calculated from the vapor pressure for H_2O from Weast et al. (1964). The HTO vapor pressures at various temperatures were fitted to an equation of the form (Sienko and Plane, 1966):

$$P_T^0 = C \exp(-\Delta H'/(R\,T)) \tag{11}$$

where $\Delta H'$ is the amount of heat (cal) required to transform one mole of HTO to the ideal gaseous state, C is a constant (1.48574×10^9 g cm^{-1} day^{-1}), T is the temperature of the marsh water (°K), and R is the universal gas constant (R=1.987 cal mol^{-1} °K). The temperature of the marsh water must be inserted into the above relation to obtain the equilibrium vapor pressure. A fifth degree polynomial with additive errors was fitted to the observed marsh water temperature with time as the independent variable to provide an empirical relation. The polynomial coefficients in order of increasing powers of time were 7.8264, -0.18997, 6.7707E-4, 9.9128E-6, -4.7705E-8, and 5.3697E-11. For later simulations, a sine curve was used to describe annual variations in water temperature.

Background levels of HTO in the atmosphere, P_T, were derived from measurements of tritium activity in water vapor. While the water vapor was being collected, relative humidity and temperature were also measured. The absolute humidity was calculated (Monteith, 1973) by the formula

$$\chi = \frac{217\ h\ e_s(T)}{T} \tag{12}$$

where χ is absolute humidity (g m^{-3}), h is the percent relative humidity, T is the temperature (°K), and $e_s(T)$ is the vapor pressure for

saturated air (mbar). The constant, 217, is derived from the necessary units conversion. Because the specific activity of water vapor was known, the weight of HTO per volume of atmosphere could be calculated by the relation 1 dpm HTO = 3.0967×10^{-16} g HTO. Hence the mass of HTO per m^3 of atmosphere times R T/M gives the vapor pressure of HTO (Monteith, 1973) where R is the universal gas constant (8.31 Joules mol^{-1} $°K^{-1}$), T is temperature in degrees Kelvin, and M is the molecular weight of HTO per mol (gm mol^{-1}). The background tritium levels were fairly constant during the study. Therefore the average value for P_T of 0.545 g cm^{-1} day^{-2} was used as input to the model.

The functions given above were used for z_w, dz_w/dt, P_T^0, and P_T, to fit the set of differential equations (9) and (10) to the observed data for marsh water and sediment layers at depths of 1, 5, 10, 15, and 20 cm by nonlinear regression. The system was solved with Euler's method of numerical integration with a time length of 0.1 day. Errors were assumed additive, normally distributed, mean zero, constant variance, independent and identically distributed. The partial derivatives with respect to the parameters were calculated numerically as discussed in White (1976:92-95). The estimated parameters were k', D, and the initial concentration of HTO in the marsh water, $W_c(0)$. Parameter values are presented in Table 1. The fitted lines plotted with the observed data are presented in Figs. 8-13.

Study of the differences between observed and predicted values (residuals) indicated a trend to underestimate HTO concentration in marsh water. This trend was not so obvious for the predictions of sediment concentrations, probably due to the higher variability in

Table 1. Estimates of the model parameters obtained by nonlinear regression for water-sediment model II.

Parameter	Estimate	Asymptotic standard error[a]
k'	32.438 dpm g^{-1} cm^{-1}	2.5058
D	0.68860 day^{-1}	0.061793
$W_c(0)$	2468.2 dpm cm^{-3}	63.550

[a]Dixon (1970).

the observed sediment data. In general, the water-sediment model provided a good representation of the system. The high resolution of the driving variables (z, dz/dt, P_T, and P_T^0) should result in good predictive capabilities when the model is used for prediction in other areas and climatic regimes.

Validation

Results of a previous study at the same location by Lehman (1973a) were available for partial validation of model II and the parameters estimated in Table 1. His study was conducted in the same marsh unit, so better agreement could be expected between the model and the observed data than with data from a different location. Lehman presented observed HTO concentrations in the marsh water through 152 days. Marsh water depths also were given and for the simulation were fitted by linear regression with time as the independent variable to

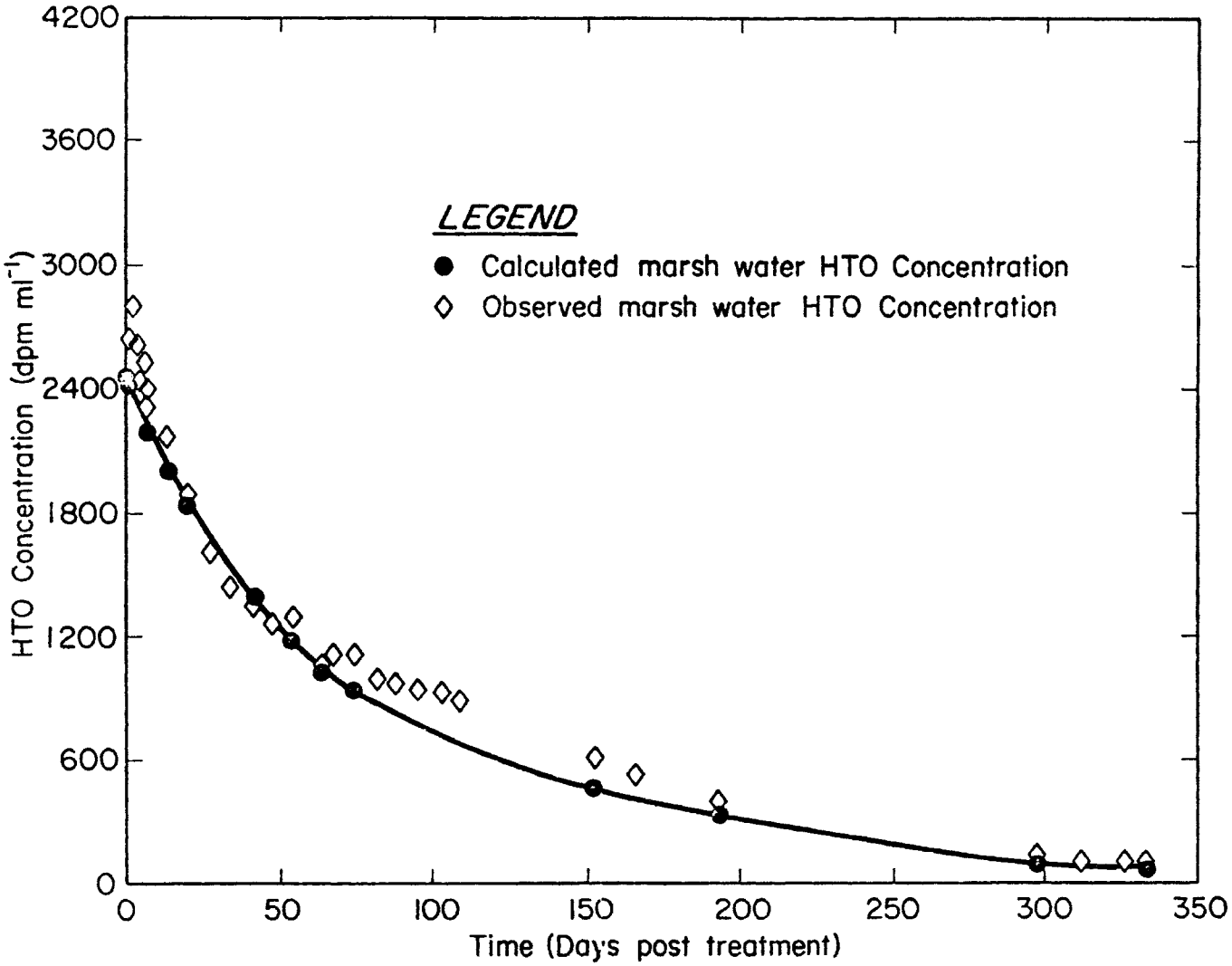

Fig. 8. Fit of water-sediment model II to the marsh water.

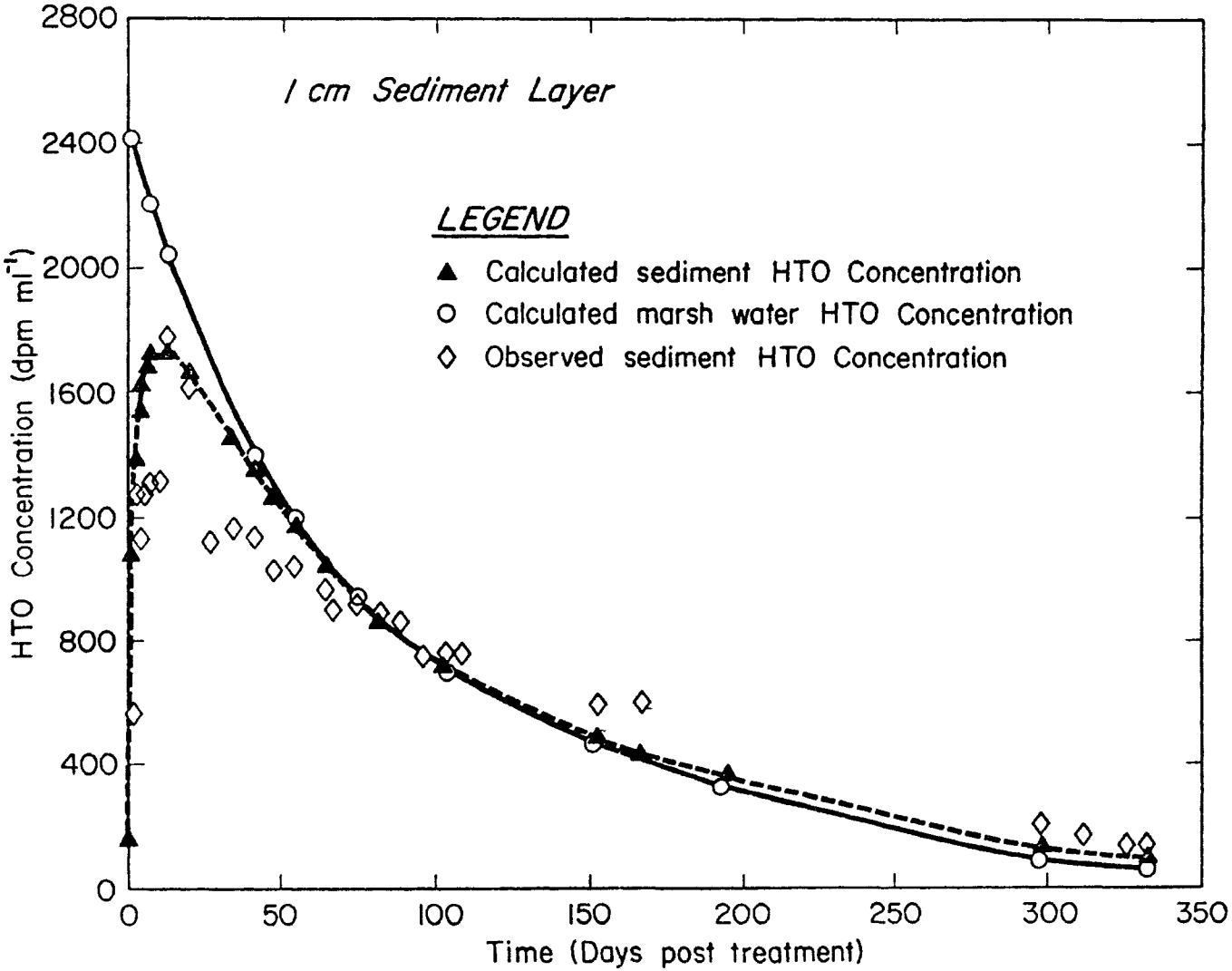

Fig. 9. Fit of the water-sediment model II to the top 1-cm sediment layer. The solid line represents the calculated marsh water HTO concentration, and the dashed line represents calculated sediment HTO concentration.

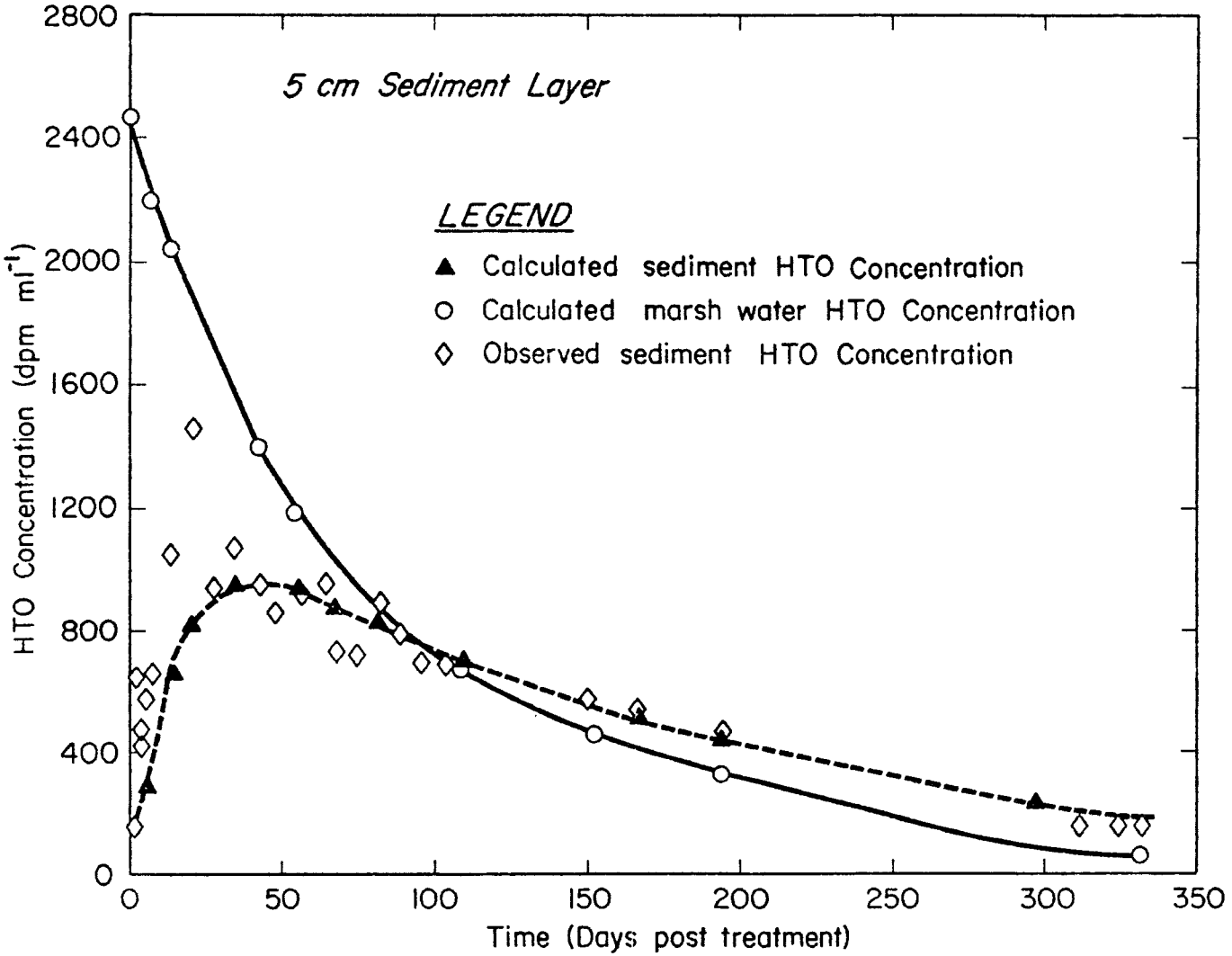

Fig. 10. Fit of the water-sediment model II to the 5-cm sediment layer. The solid line represents the calculated marsh water HTO concentration, and the dashed line represents calculated sediment HTO concentration.

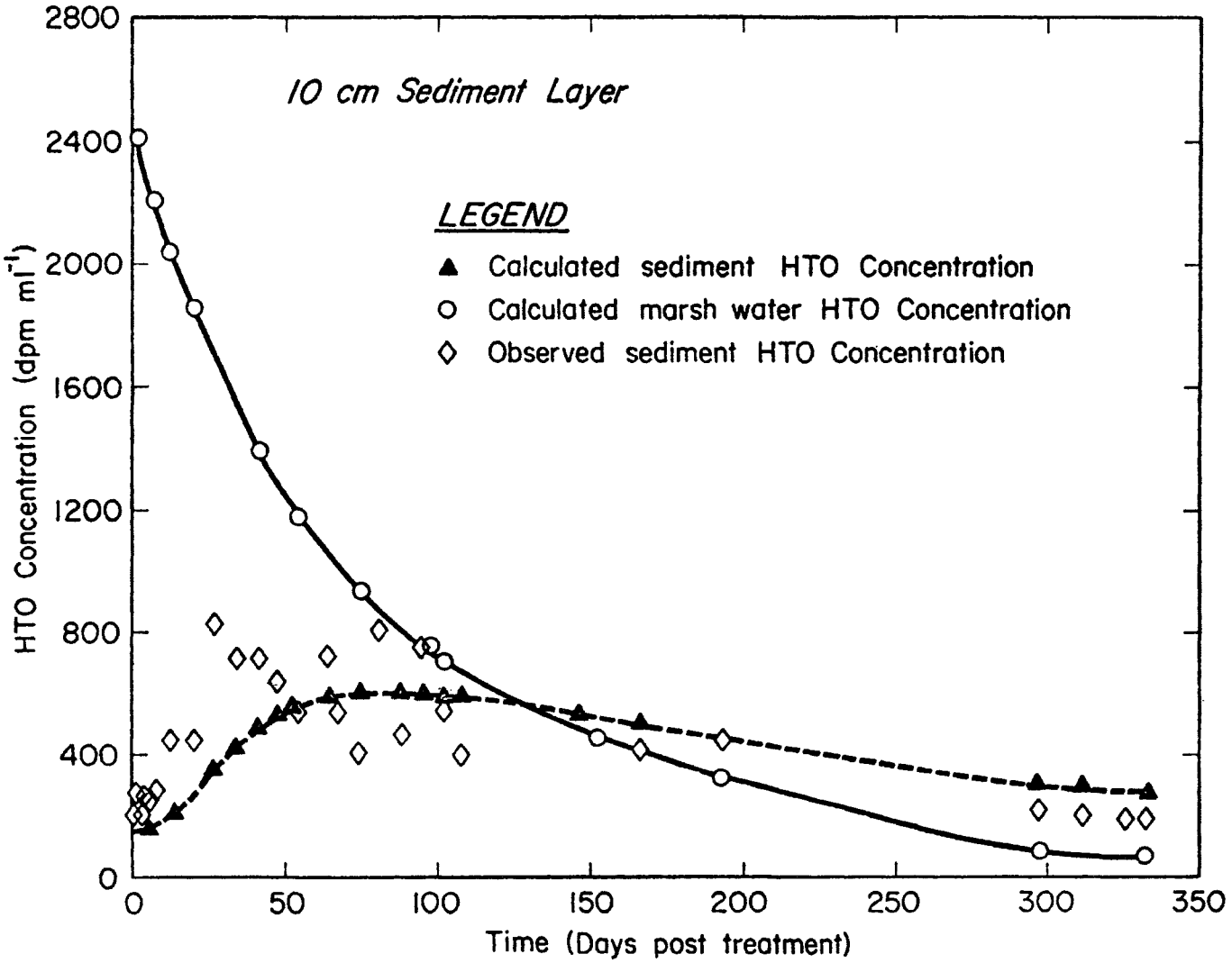

Fig. 11. Fit of the water-sediment model II to the 10-cm sediment layer. The solid line represents the calculated marsh water HTO concentration, and the dashed line represents calculated sediment HTO concentration.

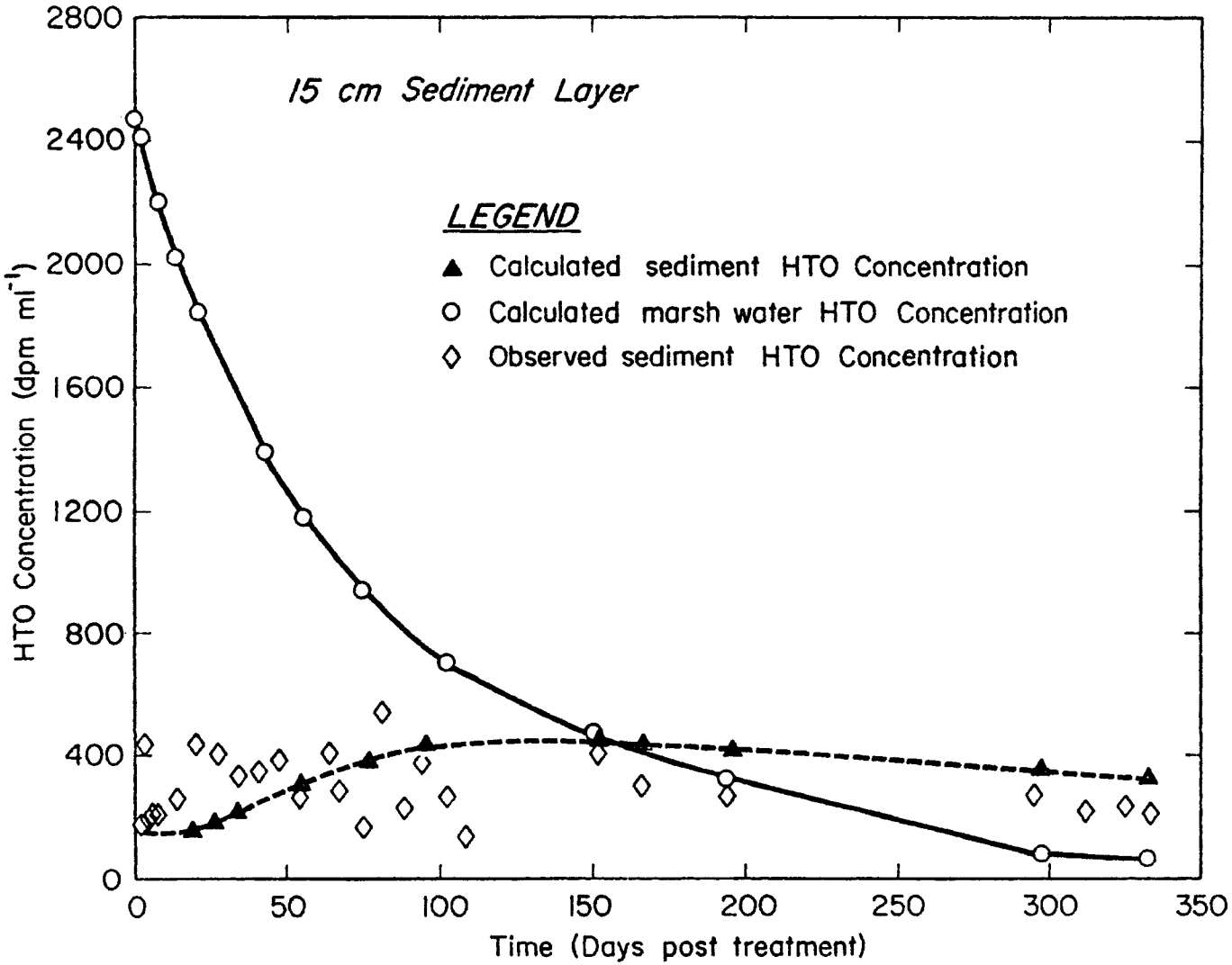

Fig. 12. Fit of the water-sediment model II to the 15-cm sediment layer. The solid line represents the calculated marsh water HTO concentration, and the dashed line represents calculated sediment HTO concentration.

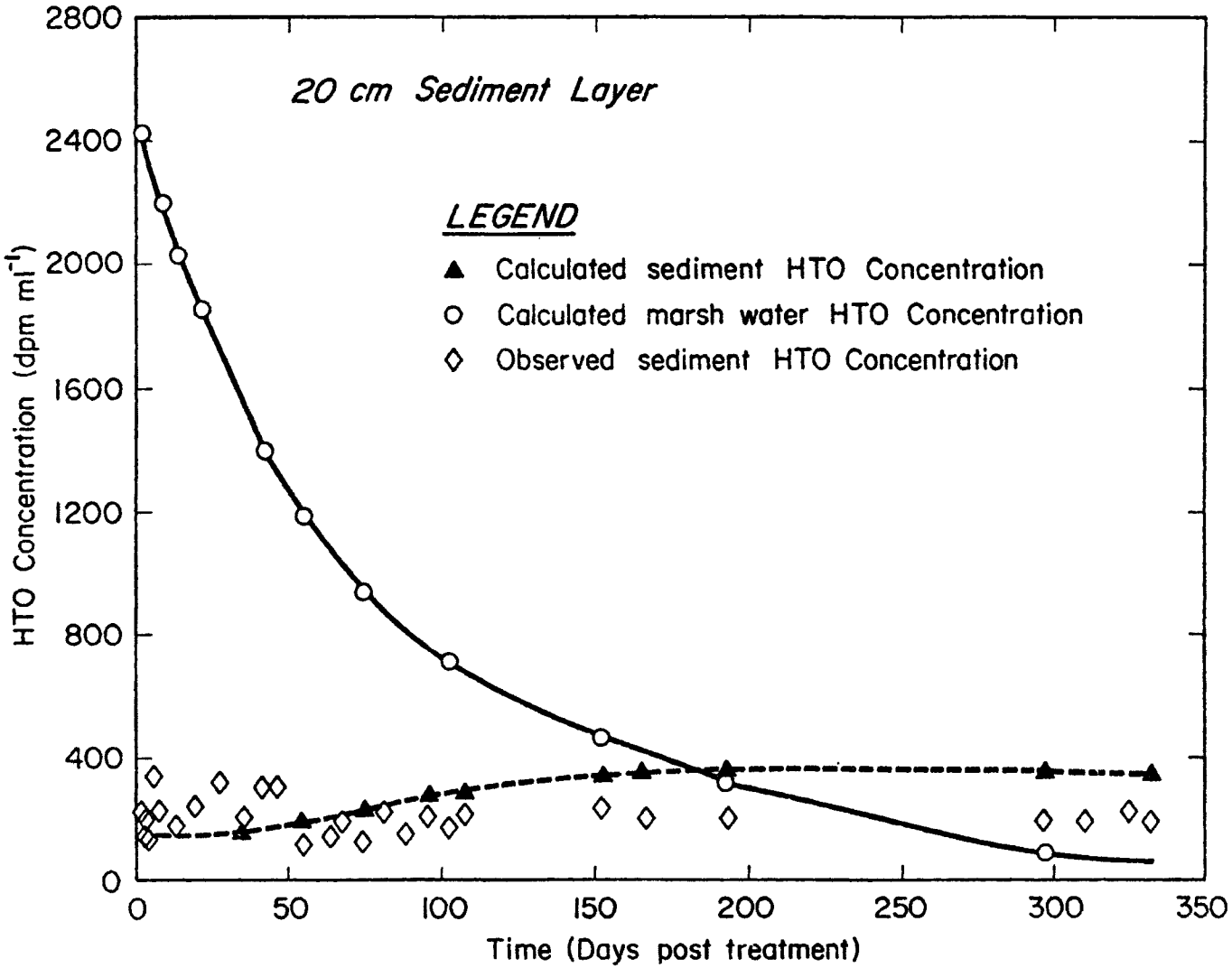

Fig. 13. Fit of the water-sediment model II to the 20-cm sediment layer. The solid line represents the calculated marsh water HTO concentration, and the dashed line represents calculated sediment HTO concentration.

provide an input function for the model. Water temperatures were calculated from a sine curve fitted to the water temperature data collected by Adams et al. (1975) with time as the independent variable. This procedure assumed that water temperature in 1972 could be approximated by water temperature in 1974. The vapor pressure of HTO in the atmosphere was assumed constant and was calculated with an average value of 25 dpm HTO cm^{-3} water vapor (Lehman, 1973b), 9.8 ml H_2O m^{-3} of atmosphere, and 15°C average air temperature, giving a value for P_T of 0.676 g day^{-2} cm^{-1}. Simulations were conducted with model II with the parameter estimates from Table 1 and the above inputs. Simulation results and observed data are presented in Fig. 14. The model provides a good prediction of observed levels.

In Model II, β is a function of the marsh water temperature, which is represented by a fifth degree polynominal in the nonlinear routine used to fit parameter values to the data. Hence no one value can be compared to the value of β presented by Horton et al. (1971). However the value of β ranges from 0.36 to 1.8 cm day^{-1} and hence brackets the value given by Horton et al. (1971) to 0.552 cm day^{-1}.

Sensitivity Analysis

Two simulations were designed to study the sensitivity of the model to the parameters estimated by nonlinear regression techniques. The constant k' was used to calculate the flow of HTO between the atmosphere and the marsh water. Simulations were run with background levels in the atmosphere $P_T = 0.5$ g cm^{-1} day^{-2}, water depth $z = 50$ cm,

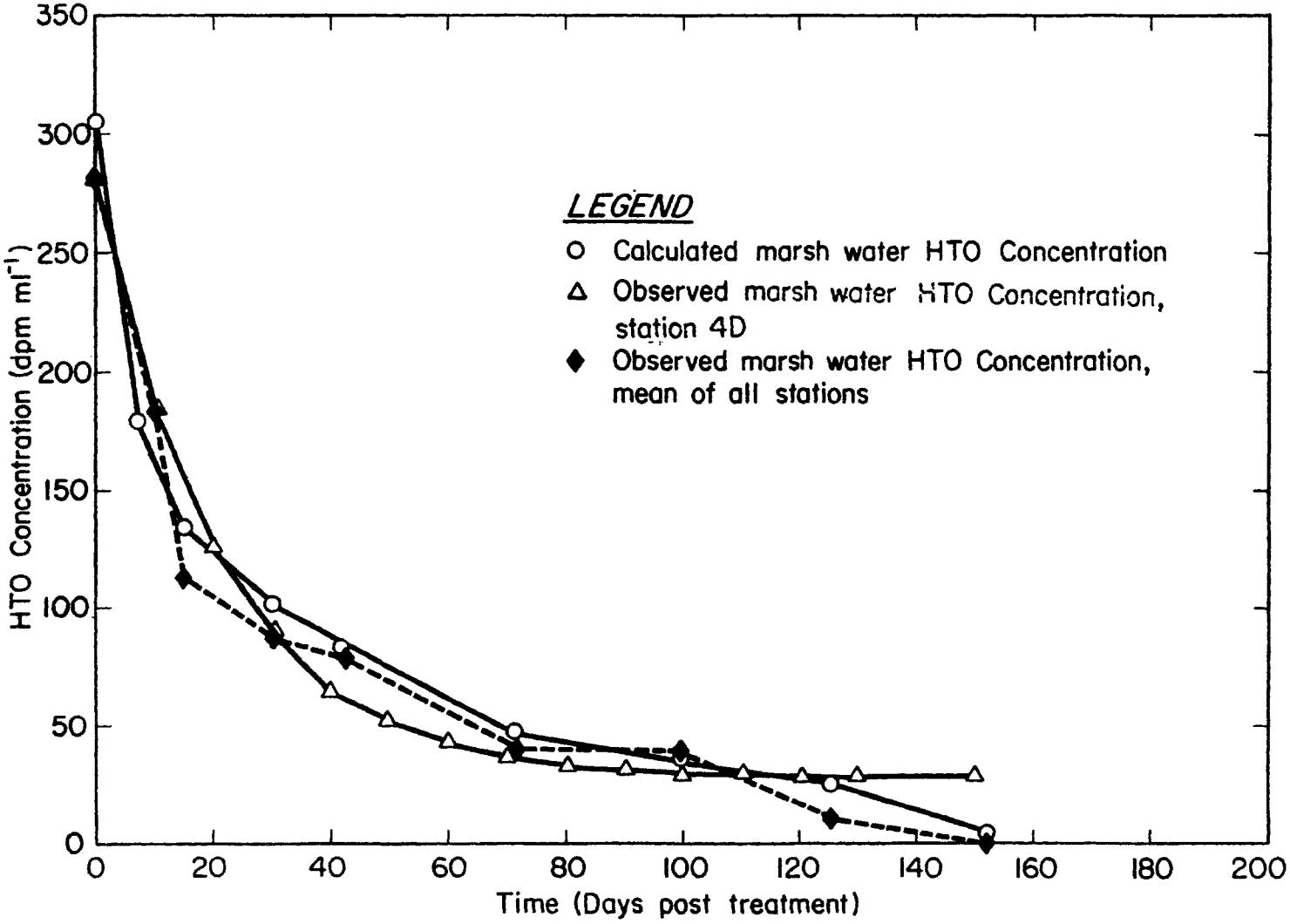

Fig. 14. Model predictions compared to observed values from Lehman (1973a). Station 4D is at the geographical center of the marsh. The area was flooded on day 150, so final observed values are not comparable to the calculated value.

change in depth $dz/dt = 0$ cm day^{-1}, and water temperature T = 20°C. Water and sediment compartments were set to zero to find how changing k' would affect the equilibrium concentration of HTO. Results are given in Table 2. A 10 percent change in k' changed the equilibrium value of the marsh water less than 0.1 percent, so that k' had a very small effect on equilibrium values.

Simulations also were conducted to study the effect of changes in the sediment diffusion coefficient, D, (day^{-1}) on model performance. The model was constructed so that with constant input, all sediment and water compartments had the same equilibrium value. Therefore changes in D would not change the equilibrium value of sediment concentrations but, rather, the rate at which the equilibrium is reached. Hence some criteria were required to measure changes in model behavior. For this analysis, the times for the 20-cm sediment compartment to reach half of the equilibrium value and for the mass of HTO in the sediment to reach half of the equilibrium value were used. For the simulation, a constant concentration in the marsh water compartment, with no atmospheric loss, was assumed. Results are presented in Table 3. A 10 percent change in D caused approximately a 10 percent change in the two criteria, so the model was fairly sensitive to D. Model predictions of times until peak values in the sediment should be interpreted with this sensitivity in mind.

Table 2. Sensitivity analysis for k'.

k'		Equilibrium water concentration
value	percent change	(dpm ml^{-1})
31.566	0	11.495
28.409	-10	11.485
34.723	+10	11.502

Table 3. Sensitivity analysis of sediment transfer coefficient, D.

D		20-cm sediment layer reaches 1/2 equilibrium		Total HTO in sediment reaches 1/2 equilibrium	
value day^{-1}	percent change	days	percent change	days	percent change
.68849	0	428	0	275	0
.75734	+10	389	-9.1	249	-9.5
.61964	-10	475	+11.0	306	+11.3

HTO Loss from a Contaminated Marsh

Simulation experiments were performed with Model II to determine the time necessary for a contaminated marsh to lose the HTO present. The first simulation was conducted with the assumption that no special efforts were made to remove tritium from the marsh. The only

loss was assumed to be through the water-atmosphere interface. The sediment and marsh water were considered to have uniform concentration. Marsh depth was held constant at 50 cm, and the atmospheric vapor pressure of tritium was assumed zero. The water temperature was assumed to follow a sine curve with amplitude of 12.5°C and mean of 12.5°C, hence varying between 0 and 25°C. The period of the sine curve was set at 365 days. About half of the initial amount of HTO was gone from the marsh by 150 days (Fig. 15,A). However, for the sediment, 400 days were required to remove half of the initial tritium mass.

In a second simulation, the marsh water was assumed to contain no HTO. The sediment was assumed to contain uniform concentrations to a depth of 30 cm. The marsh water was kept at zero concentration to simulate a high rate of turnover, such as occurred when water was pumped through the marsh to remove HTO from contaminated sediments. Half of the tritium originally in the sediment was removed by 275 days (Fig. 15,B). Of that remaining, half was gone by 655 days. An exponential retention curve was not expected, since the model consisted of 30 connected sediment compartments. After about 100 days, however, the curve became fairly straight on a semi-log plot, indicating that good predictions can be made with a single exponential function.

From these simulations, it was concluded that periodic replacement of the marsh water would increase significantly the rate at which HTO was removed from contaminated sediments. The best method for removing HTO from the sediments probably would be to remove all the overlying water, and allow the sediment to dry. This cannot be simulated with the model, however.

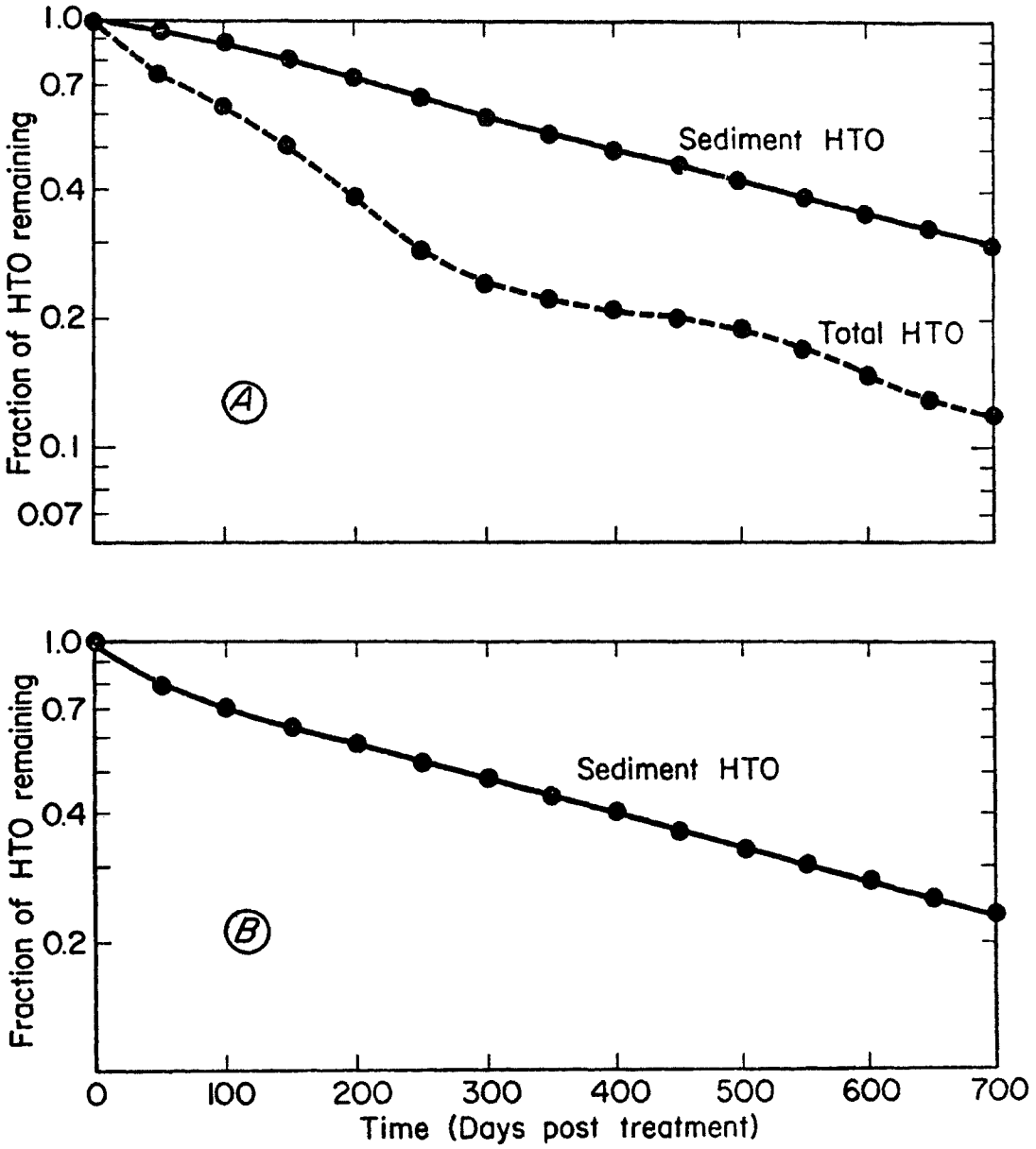

Fig. 15. Simulation of HTO loss from a contaminated marsh. A represents loss only through the marsh water - atmosphere interface, whereas B represents the loss of HTO from the sediment when the marsh water is constantly being replaced.

The model can be used experimentally to find methods to increase the loss rate of HTO from water bodies. One such manipulation might be to raise the marsh water temperature. Simulations were conducted by changing the parameter values of the sine curve describing the marsh water temperature. Heating of the marsh was assumed to take place only during the cooler portion of the year. The sine curve was modified so that the maximum temperature during the summer was the same for all simulations. The minimum temperatures during the winter were increased the most. Changing the marsh temperature in this fashion would tend to cause the least environmental impact because levels of dissolved oxygen in the summer would not be lowered. Background levels of tritium in sediment and atmosphere were assumed zero.

Simulations showing no increase, 5°C increase, and 10°C increase for the lowest winter temperature are shown in Table 4. The results show that raising the marsh temperature during the winter months may provide a feasible method of increasing the loss rate of HTO. Raising the minimum winter temperature 10°C will halve the time for 50 percent of the HTO initially present to be lost from the marsh. Note, however, that these simulations had a 29 October starting date, so that increasing the winter water temperature will tend to show a greater effect than if the simulation assumed a spring starting date.

Uptake of Atmospheric HTO by the Marsh System

Simulations were conducted to determine the equilibrium concentrations of HTO in the marsh when the atmosphere is the only tritium source. Values of P_T simulated were 0.25, 0.5, 0.75, 1.0 and 1.5

Table 4. Effect of heating the marsh water to increase HTO loss to the atmosphere.

Maximum increase (°C)	Sine curve mean	Sine curve amplitude	No. of days until fraction of initial remains 1/2	1/4	1/8	Fraction remaining after 250 days	500 days	750 days	1000 days
0	12.196	12.738	84	186	228	0.0941	0.046	0.027	0.017
5	14.696	10.238	58	141	199	0.069	0.035	0.021	0.013
10	17.196	7.738	42	100	164	0.049	0.026	0.016	0.010

gm cm^{-1} day^{-2}. With an assumed relative humidity of 74 percent and an average temperature of 11°C, these values corresponded to 12, 24, 36, 48, and 72 dpm ml^{-1} of water vapor. The average background level of HTO in the water vapor given by Lehman (1973b) was 25 dpm ml^{-1}, and Adams (personal communication) found the values ranged from 0 to 53 dpm ml^{-1}.

Results of the simulations are given in Table 5. The HTO concentration in water fluctuates because of the change in water temperature. As previously discussed, the equilibrium vapor pressure is a function of the water temperature. Hence because water temperature is calculated from a sine wave, the water concentration likewise follows a periodic function. The sediment compartments also vary in a periodic fashion, but with an increasingly smaller amplitude with increasing sediment depth. The mean concentration over the year for all

compartments would be the average of the minimum and maximum values presented in Table 5.

Table 5. Uptake of HTO by the marsh system from the atmosphere. The maximum and minimum values are of the equilibrium water concentration curve for the value of P_T. The fluctuation is due to the water temperature cycle.

P_T (gm cm^{-1} day^{-2})	Min. concentration (dpm ml^{-1})	Max. concentration (dpm ml^{-1})
0.25	4.9	14.5
0.50	9.9	28.9
0.75	14.8	43.4
1.0	19.7	57.8
1.5	29.6	86.8

ORGANISM MODEL

An organism was conceptualized as a two compartment system. The first compartment was the body water, with tritium contained at HTO. This compartment was termed the unbound compartment. A second compartment was assumed to contain all tritium not in the form of HTO, and was referred to as the bound compartment. The only source of tritium to the organism was assumed to be marsh water. Hence the system was compartmentalized as in Fig. 16. This model was developed under the assumption that the marsh water compartment could be explained adequately by a single exponential. As shown in the development of the water-sediment model II, this was an oversimplification. However, this simplification allowed an analytic solution to be obtained for the three-compartment system described.

The differential equations used to describe the compartment system in Fig. 16 were:

$$\frac{dW_c}{dt} = -a\ W_c \tag{13}$$

$$\frac{dU}{dt} = b\ W_c - (f+c)\ U + d\ B \tag{14}$$

$$\frac{dB}{dt} = f\ U - (d+g)\ B \tag{15}$$

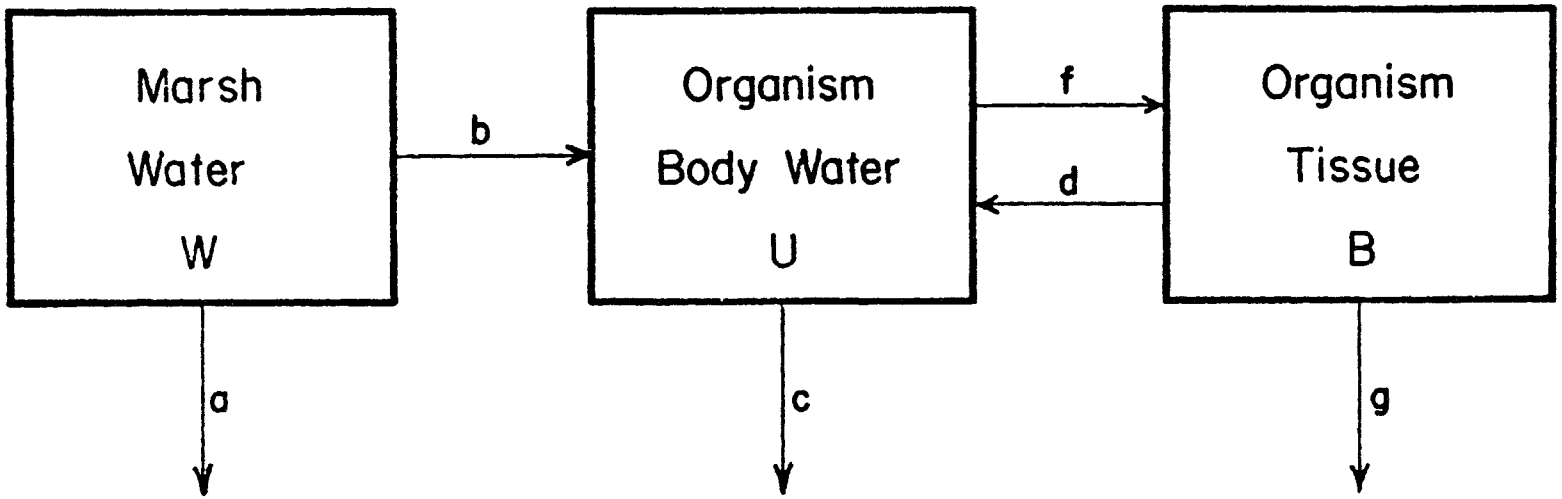

Fig. 16. Compartment model of tritium kinetics in the marsh organisms.

where W_c is the marsh water HTO concentration (dpm g H^{-1}), $W_c > 0$,

U is the organism water HTO concentration (dpm g H^{-1}), $U \geq 0$,

B is the organism tissue tritium concentration (dpm g H^{-1}), $B \geq 0$,

a is the loss rate constant for HTO escaping to the atmosphere (day^{-1}), $a > 0$,

b is the transfer constant from the marsh water to the organism unbound compartment (day^{-1}), $b > 0$,

c is the loss rate constant for the organism unbound compartment (day^{-1}), $c > 0$,

d is the transfer constant from the bound to the unbound compartment (day^{-1}), $d > 0$,

f is the transfer constant from the organism unbound to bound bound compartment (day^{-1}), $f > 0$,

g is the loss rate constant for the organism bound compartment, $g > 0$, and

t is the time (days).

Laplace transforms were used to solve this set of differential equations; it was assumed that initial concentrations in the unbound and bound compartments were zero. These solutions are:

$$W_c(t) = W_c(0) \exp(-a\,t) \tag{16}$$

$$U(t) = b\,W_c(0)\left\{\frac{(\lambda_1+d+g)\,e^{\lambda_1 t}}{(\lambda_1-\lambda_2)(\lambda_1+a)} + \frac{(\lambda_2+d+g)\,e^{\lambda_2 t}}{(\lambda_2-\lambda_1)(\lambda_2+a)} + \frac{(-a+d+g)\,e^{-at}}{(-a-\lambda_1)(-a-\lambda_2)}\right\} \tag{17}$$

$$B(t) = f\,b\,W_c(0)\left\{\frac{e^{\lambda_1 t}}{(\lambda_1-\lambda_2)(\lambda_1+a)} + \frac{e^{\lambda_2 t}}{(\lambda_2-\lambda_1)(\lambda_2+a)} + \frac{e^{-at}}{(-a-\lambda_1)(-a-\lambda_2)}\right\} \tag{18}$$

where

$$\lambda_1 = \frac{-(c+d+f+g) + \sqrt{(c+d+f+g)^2 - 4(cd+cg+fg)}}{2}$$

$$\lambda_2 = \frac{-(c+d+f+g) - \sqrt{(c+d+f+g)^2 - 4(cd+cg+fg)}}{2}$$

A major simplification of the organism model was that the only source of input to the bound compartment was from the unbound compartment. For autotrophs this assumption is probably valid. To illustrate, consider the photosynthesis reaction. The chemical equation for photosynthesis can be written simply:

$$6CO_2 + 6H_2O + 672\ \text{kcal} \longrightarrow C_6H_{12}O_6 + 6O_2$$

The water required by the reaction would come from the organism's body water, that is, the unbound compartment. The above equation implies that if tritiated water is supplied, tritiated glucose results.

However, for heterotrophs this tritiated glucose will be consumed and utilized. In terms of the compartment model, this implies a source of tritium reaching the bound compartment that is not routed through the unbound compartment. Rosenthal and Stewart (1971) shows that *Lymnaea reflexa* and *Helisoma trivolvis* snails fed tritiated algae for 6 months incorporated significantly more bound tritium than those living on non-tritiated algae. They felt that the content of the bound compartment is directly proportional to the tritium content of the food assimilated and transformed into animal tissues and to tritium-protium isotopic exchange. Therefore the outside sources of bound tritium should be assumed significant.

This relationship is difficult to model, however. An arbitrary function to describe the bound levels in food could be used, but this probably would not increase the validity of the model. A second approach might be to assume a particular heterotroph is feeding solely on a particular autotroph. Then, after fitting the model parameters to the autotroph data, assume this function could be used as input to the heterotrophs. However, the set of differential equations would be sufficiently difficult that analytical solutions would be more complex, requiring a numerical solution for this study. The second and primary reason an attempt was not made to fit a heterotroph in this fashion was that plant data from the marsh were not available.

Therefore a third approach was used to model the input of bound tritium to a heterotroph, that is, the bound loss rate coefficient was made negative. A negative g implied that the net rate of change of the bound compartment was an uptake of bound tritium from an outside source.

Hence the net uptake rate of bound tritium is proportional to the amount of bound tritium present. This relationship does not make sense in terms of a predator taking prey, since the implication is that the predator takes the prey irrespective of prey availability. However, the amount of bound tritium incorporated by a heterotroph would be expected to be proportional to the amount of bound tritium present in the food. Since the best data available for this study on bound tritium in the marsh were from crayfish, it is reasonable to assume that the uptake of bound tritium was a function of the bound tritium compartment. This approach also greatly simplified the estimation procedure.

The values for $W_c(0)$ and a were estimated from a single exponential fitted to the marsh water compartment (water-sediment model I). This left five parameters to be estimated from the observed crayfish data: b, c, d, f, and g. Equations (17) and (18) were fitted simultaneously to minimize the sum of squared residuals for both the unbound and bound compartments. Hence the parameter estimates reflected both the unbound and bound observations. Sampling errors were assumed to be additive to equations (17) and (18), normally distributed, mean zero, constant variance, independent, and identically distributed. Partial derivatives were calculated analytically (White, 1976:92-95).

The values of the estimated parameters are given in Table 6, and the observed data and fitted line are plotted in Figs. 17-18. The bound tritium taken up from outside the organism comprised most of the compartment contents as indicated by the magnitude of g. The low value for parameter f indicated that most tritium in the bound compartment came from food.

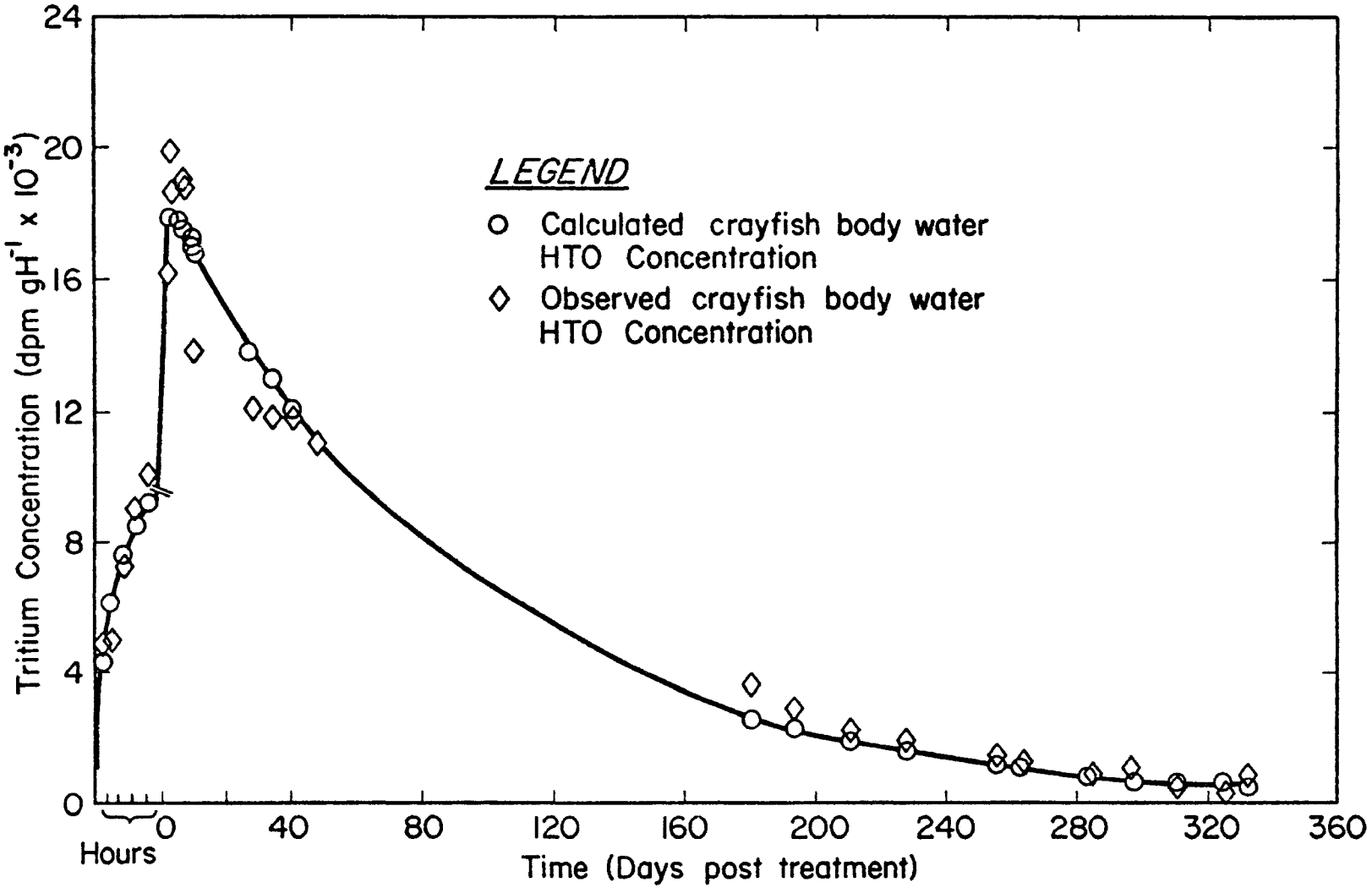

Fig. 17. Fit of organism model to observed HTO concentration in crayfish body water.

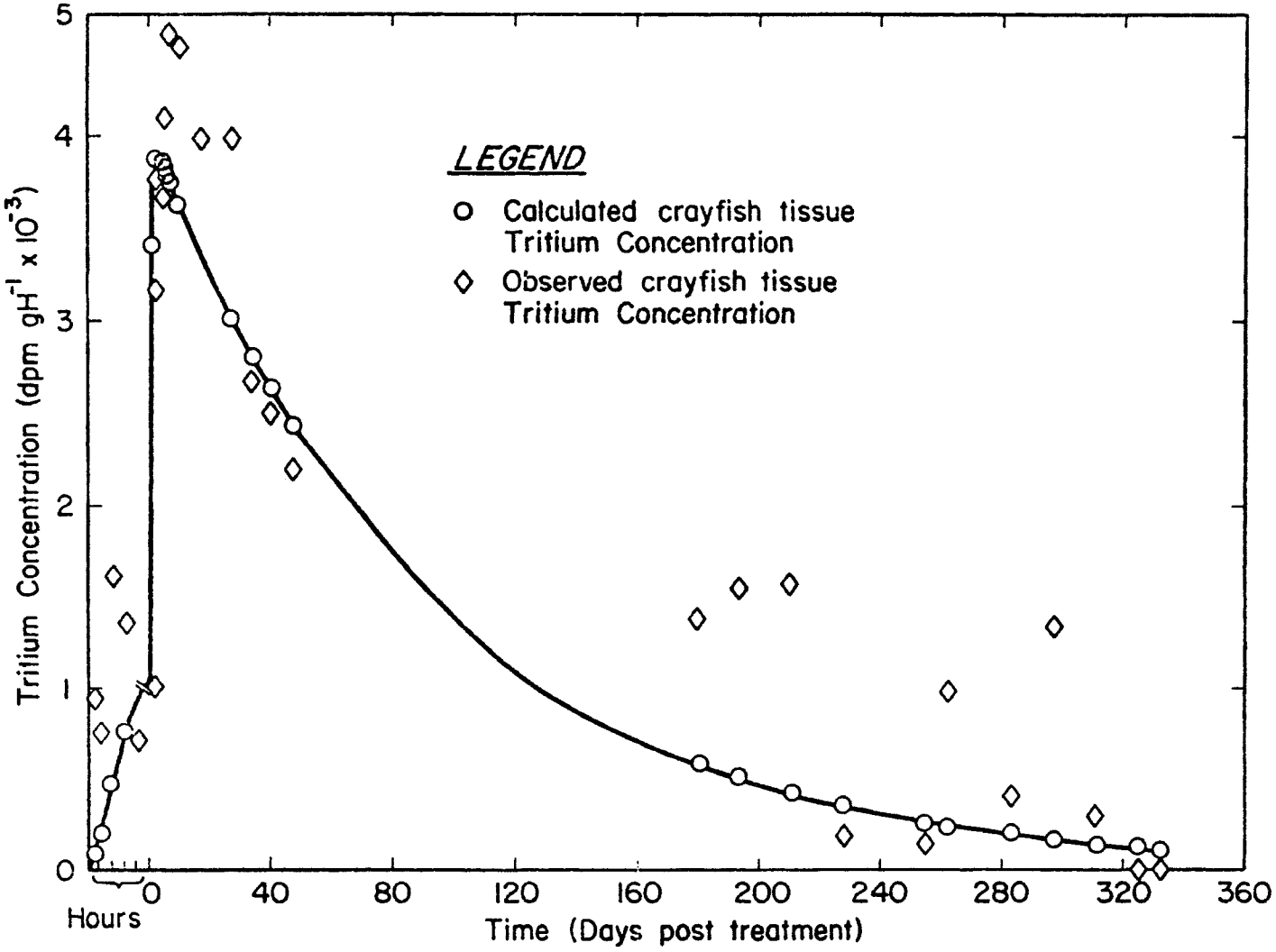

Fig. 18. Fit of organism model to observed tritium concentration in crayfish tissue.

Table 6. Estimated values of model parameters for the crayfish model.

Parameter	Value	Asymptotic standard error[a]
b	14.538	2.0508
c	47.763	4.3507
d	144.29	NE[b]
f	1.2617	0.04254
g	-138.47	1.8868

[a]Dixon (1970).

[b]Standard error was not estimated due to an ill-conditioned variance-covariance matrix.

A crude measure of the goodness of fit of the model to the observed data can be made because each observation is actually the mean of three to four samples. Hence the mean squared error for the individual observations about the mean for each time (pure error) can be calculated from the samples to estimate the sampling variance, which for the crayfish data was 1,166,740. The mean squared error for the fitted model was also an estimate of the sampling variance, which for the crayfish model was 962,230. However, Draper and Smith (1966) pointed out that for nonlinear least squares in general, the mean squared error does not lead to an unbiased estimate of the variance as in the linear case. An approximate idea of the fit of the model can be obtained, however, since the methods should give similar values. For the crayfish data, the model appears to provide an adequate fit.

Other investigators (Stewart et al., 1971); Rosenthal and Stewart, 1961) have shown that the organism's unbound compartment approaches the marsh water concentration at equilibrium conditions. For the marsh water to be held constant implies that a = 0. Hence with a = 0,

$$\lim_{t \to \infty} U(t) = \frac{(d + g)\ b\ W(0)}{(-\lambda_1)\ (-\lambda_2)}$$

$$= \frac{(d + g)\ b\ W(0)}{(cd + cg + fg)}$$

For the limit to equal W(0) implies

$$\frac{(d + g)\ b}{(cd + cg + fg)} = 1$$

or

$$b = \frac{(cd + cg + fg)}{(d + g)}$$

Hence building into the model the additional information that the unbound compartment reaches the same equilibrium value as the marsh water implies substituting the above relation for b.

From the parameter estimates given in Table 6, the asymptotic value of the unbound compartment was 82 percent of the marsh water concentration, not the expected value of 100 percent. The major reason that the parameter values did not give a value of one probably was because the data were biased. Preparation of the samples allowed contact with the atmosphere. Because HTO would evaporate differentially to water, some HTO would be lost. Also, HTO would be lost from a frozen sample during storage. Hence the value of 82 percent probably is

very realistic for the present data. Therefore, the model has not been modified to incorporate equation (19), because this probably would bias the estimates of the remaining parameters. If the value of 82 percent is due to random error, however, then the remaining parameters could be estimated more efficiently by incorporating equation (19).

The bound compartment approaches a value of about 18 percent of the water compartment. This value seems realistic, and compares with a value of 25 and 26 percent for the snails *Lymnaea reflexa* and *Helisoma trivolvis*, respectively (Stewart et al., 1971). Other investigators, however, have found much larger values. Rosenthal and Stewart (1971) found values from 50 to 69 percent for the same two species of snails. Patzer et al. (1973) found values from 74 to 92 percent for mosquito fish *(Gambusia affinis)* in a tritiated environment for 93 days. Adams (personal communication) has shown that various methods of sample preparation to obtain the bound fraction give different results. Hence laboratory technique may explain much of the discrepancy in the published literature.

Another assumption that could be incorporated into the organism model is that the bound compartment also reaches an equilibrium that is some fraction of the marsh water equilibrium. The limit with a = 0 is

$$\lim_{t \to \infty} B(t) = \frac{f\ b\ W(0)}{cd + cg + fg}$$

If $B(\infty) = W(0)$, then

$$b = \frac{cd + cg + fg}{f}$$

If the assumption is made that $U(\infty) = W(0)$, and $b = (cd + cg + fg)/(d + g)$, this information also can be incorporated. Hence $f = d + g$ if $W(0) = U(\infty) = B(\infty)$.

The same analysis can be obtained with only the differential equations. At equilibrium, all derivatives must be equal to zero, that is, for any compartment, the sum of the inputs equals the sum of the outputs when the compartment is in equilibrium. Hence substituting in the unbound and bound equations, $U(\infty) = W(0)$, and subtracting the equations to remove $B(\infty)$ gives with manipulation

$$b = \frac{cd + cg + fg}{d + g}$$

Then substituting this expression into either the unbound or bound equation gives

$$B(\infty) = \frac{f\ W(0)}{d + g}$$

Hence analytical solutions are not required to incorporate additional information on equilibrium concentrations into the model.

PARAMETER ESTIMATION ASSUMING BOTH PROCESS AND SAMPLING VARIATION

Single Compartment

The differences between the observed values and the predicted values were assumed due to sampling errors in fitting the models described previously to the observed data. That is, the true value of the process is not observable, so that the observed value had an attached sampling error. Hence, the estimates of the parameters were selected such that the sum of squares of the sampling errors was minimized.

If the observed process also contains some random variation, denoted here as process variation, a process perturbation at time t also affects all future observations of the process and hence generates an autocorrelated sequence of residuals. The model cannot predict the observed values exactly, not only because there is some attached sampling error, but also randomness in the real process. Hence when the sum of squared residuals is minimized, this autocorrelated random error is treated as sampling error, and is not recognized as process variation. The validity of the parameter estimates will depend on the relative magnitude of the two types of variation, and the magnitude of the autocorrelation in the residuals. The process variations are not observable, so the investigator must assume that the sampling variation is much larger than the process variation to conclude that the parameter estimates are correct. In the following section, a method has been

developed to estimate parameter values for compartmental models when both process and sampling variation are thought significant.

First assume a single compartment with concentration I_n at time $t = 0$. Then the equation describing the loss of material from the compartment when a constant loss coefficient is assumed is

$$\frac{d\,W(t)}{dt} = -\,k\,W(t) + e(t) \tag{20}$$

where $W(t)$ is the concentration at time t, and $e(t)$ is the process variation or the perturbation in the rate of change of $W(t)$. Assume the compartment is observed at times t_i, $i = 0, 1, \ldots, n$, and that $t_0 = 0$. For the time period $t_i - t_{i-1}$, assume $e(t) = a_i$, or that the rate error can be approximated by a constant over the period between observations. Also let a_i, $i = 1, \ldots, n$ be a random variable normally distributed with mean zero and variance σ_a^2, with all values mutually independent. Then

$$e(t) = a_i[\mu(t - t_{i-1}) - \mu(t - t_i)]$$

where $\mu(x)$ is Heaviside's unit function. Taking the Laplace transform of equation (20) gives

$$s\,W(s) - I_n = -k\,W(s) + \sum_{i=1}^{\ell} \frac{a_i}{s}\,[\exp(-s\,t_{i-1}) - \exp(-s\,t_i)]$$

where ℓ equals the i satisfying $\min(t_i) > t$, i.e., $t_\ell = \min(t_i) > t$, and I_n is the initial compartment concentration. Thus applying the convolution theorem,

$$W(t) = I_n \exp(-kt) + \sum_{i=1}^{\ell} \int_0^t \exp(-k u)\, a_i \,[\mu(t - u - t_{i-1})$$

$$- \mu(t - u - t_i)]\ du$$

When the variable of integration is changed,

$$W(t) = I_n \exp(-kt) + \sum_{i=1}^{\ell} \int_0^t \exp(-k(t-u))\, a_i$$

$$\cdot\ [\mu(u-t_{i-1}) - \mu(u-t_i)]\ du$$

Therefore the compartment concentration at time t is given by

$$W(t) = I_n \exp(-kt) + \exp(-kt) \sum_{i=1}^{m} \frac{a_i}{k} [\exp(kt_i) - \exp(kt_{i-1})]$$

$$+ \exp(-kt) \left[\frac{a_{m+1}}{k} (\exp(kt) - \exp(kt_m))\right] \qquad (21)$$

where m is chosen such that $t_m = \max(t_i) < t$.

Assume now that the true concentration value of the compartment at t_i is not observed, but includes a sampling error b_i, where b_i is some sampling error for the i^{th} observation ($i=0, \ldots, n$, where $n+1$ observations are taken). Assume the b_i values are normally distributed with mean zero and variance σ_b^2, and all values are mutually independent. Then the model for the observed compartment concentration at time t_i is

$$W(t_i) = I_n \exp(-kt_i) + \frac{\exp(-k\, t_i)}{k}$$

$$\cdot \sum_{j=1}^{i} a_j [\exp(kt_j) - \exp(kt_{j-1})] + b_i \qquad (22)$$

Substituting the relationship

$$W(t_{i-1})-b_{i-1} = I_n \exp(-kt_{i-1}) + \frac{\exp(-kt_{i-1})}{k}$$

$$\cdot \sum_{j=1}^{i-1} a_j \left[\exp(kt_j)-\exp(kt_{j-1})\right]$$

into equation (22) gives a simplified expression for the observed concentration at time t_i

$$W(t_i) = \exp(-k(t_i-t_{i-1}))\ (W(t_{i-1})-b_{i-1}) + \frac{a_i}{k}\ [1-\exp(-k(t_i-t_{i-1}))] + b_i \qquad (23)$$

where $W(t_0)$ is the observed initial value of the concentration (t_0=0). Solving for a_i gives the expression in terms of b_i

$$a_i = \frac{k}{1-\exp(-k(t_i-t_{i-1}))}\ \{W(t_i) - b_i - \exp(-k(t_i-t_{i-1}))$$

$$\cdot\ (W(t_{i-1}) - b_{i-1})\} \qquad (24)$$

Equation (23) describes the model for which a maximum likelihood estimate for k is to be obtained. Because the a_i (i=1, 2, ..., n) and b_i (i=0, 1, ..., n) are assumed normally distributed, mean zero, and with unknown variance σ_a^2 and σ_b^2 respectively, the following likelihood function is taken

$$L = \prod_{i=1}^{n} (2\Pi\sigma_a^2)^{-1/2} \exp\ (-a_i^2/2\sigma_a^2) \prod_{i=0}^{n} (2\Pi\sigma_b^2)^{-1/2} \exp(-b_i^2/2\sigma_b^2)$$

Taking logarithms of L provides

$$\ln L = \sum_{i=1}^{n} [-1/2 \ln(2\Pi\sigma_a^2) - a_i^2/2\sigma_a^2]$$

$$+ \sum_{i=0}^{n} [-1/2 \ln(2\Pi\sigma_b^2) - b_i^2/2\sigma_b^2]$$

The variances σ_a^2 and σ_b^2 were assumed unknown. Hence expressions for these must be determined and substituted into the above expression before ln L can be maximized. Taking the derivative of ln L with respect to σ_a^2 gives

$$\frac{\partial \ln L}{\partial \sigma_a^2} = \frac{-n}{2} \quad \frac{1}{\sigma_a^2} - \sum_{i=1}^{n} -a_i^2/2(\sigma_a^2)^2$$

Setting this result to zero and solving for an expression for σ_a^2 gives

$$n \sigma_a^2 = \sum_{i=1}^{n} a_i^2$$

implying that σ_a^2 is estimated by the expression

$$\sigma_a^2 = \sum_{i=1}^{n} a_i^2/n$$

An analogous procedure produces the similar estimate for σ_b^2:

$$\sigma_b^2 = \sum_{i=0}^{n} b_i^2 \; / \; (n+1)$$

Substitution of the above maximum likelihood estimates into the likelihood functions shows that L is minimized when $(\sum_{i=1}^{n} a_i^2)$ $(\sum_{i=0}^{n} b_i^2)$

is minimized. However this minimum can be easily achieved by letting $a_i=0$ for all i and having all sampling error. In addition, the minimum is also achieved when $b_i = 0$ for all i and having all process variation. Hence maximum likelihood estimates for the combined process variation and sampling error model are only achieved when either the process variations are set to zero ($\sigma_a^2=0$) or sampling errors are set to zero ($\sigma_b^2=0$). Maximum likelihood estimates for k do not exist when either all the a_i or all the b_i are not assumed equal to zero, or $\sigma_a^2\neq 0$ and $\sigma_b^2\neq 0$.

Hence a second method of parameter estimation, least squares, has been used in an attempt to find estimators for the case when all the a_i or all the b_i are not assumed equal to zero. Least squares estimators have no general optimum properties to recommend them, even asymptotically, such as maximum likelihood estimators have (Kendall and Stuart, 1967). However, in an extremely important case, least squares does have the optimum property, even in small samples, that it provides unbiased estimators which have minimum variance. This situation is usually described as the linear model, in which observations are distributed with constant variance about (possibly differing) mean values that are linear functions of the unknown parameters, and in which the observations are all uncorrelated in pairs (Kendall and Stuart, 1967). Unfortunately this property has not been shown to extend to nonlinear models such as considered here.

Parameter values which minimize SS

$$SS = \sum_{i=1}^{n} a_i^2 + \sum_{i=0}^{n} b_i^2 \qquad (25)$$

provide least squares estimates of the parameters. Substituting equation (24) for a_i into equation (25) gives

$$SS = \sum_{i=1}^{n} \frac{k^2}{(1-\exp(-k(t_i-t_{i-1})))^2} \{(W(t_i)-b_i)^2 + (W(t_{i-1}) - b_{i-1})^2 \cdot$$

$$\exp(-2k(t_i-t_{i-1}))-2 \exp(-k(t_i-t_{i-1})) (W(t_{i-1})-b_{i-1})(W(t_i)-b_i)\}$$

$$+ \sum_{i=0}^{n} b_i^2 \qquad (26)$$

Equation (26) reduces the total sum of squares, which is to be minimized, to an equation involving parameter values and the unknown sampling errors. The values of the sampling errors, b_i, $i = 0, 1, \ldots, n$, which will minimize the sums of squares and thus give least squares estimates of the unknown parameters, can be found by differentiating equation (26) with respect to b_i, $i=1, 2, \ldots, n-1$, and setting the results to zero. When the results are divided by $2k^2$, the following recursive expression is obtained:

$$\frac{-b_{i-1}}{2\cosh(k(t_i-t_{i-1}))-2} + b_i \{\frac{1}{k^2} + \frac{\exp(k(t_i-t_{i-1}))}{2\cosh(k(t_i-t_{i-1}))-2}$$

$$+ \frac{\exp(-k(t_{i+1}-t_i))}{2\cosh(k(t_{i+1}-t_i))-2} \} - \frac{b_{i+1}}{2\cosh(k(t_{i+1}-t_i))-2}$$

$$= \frac{-W(t_{i-1})}{2\cosh(k(t_i-t_{i-1}))-2} + W(t_i)\left\{\frac{\exp(k(t_i-t_{i-1}))}{2\cosh(k(t_i-t_{i-1}))-2}\right.$$

$$\left. + \frac{\exp(-k(t_{i+1}-t_i))}{2\cosh(k(t_{i+1}-t_i))-2}\right\} - \frac{W(t_{i+1})}{2\cosh(k(t_{i+1}-t_i))-2} \qquad (27)$$

By the same procedure, the partial derivative of SS with respect to b_0 provides the expression

$$\left(\frac{1}{k^2} + \frac{\exp(-k\ t_1)}{2\cosh(kt_1)-2}\right) - \frac{b_1}{2\cosh(kt_1)-2}$$

$$= \frac{W(t_0)\exp(-kt_1)}{2\cosh(kt_1)-2} - \frac{W(t_1)}{2\cosh(kt_1)-2} \qquad (28)$$

Likewise the partial derivative of SS with respect to b_n provides

$$\frac{-b_{n-1}}{2\cosh(k(t_n-t_{n-1}))-2} + b_n\left(\frac{1}{k^2} + \frac{\exp(k(t_n-t_{n-1}))}{2\cosh(k(t_n-t_{n-1}))-2}\right)$$

$$= \frac{-W(t_{n-1})}{2\cosh(k(t_n-t_{n-1}))-2} + \frac{W(t_n)\exp(k(t_n-t_{n-1}))}{2\cosh(k(t_n-t_{n-1}))-2} \qquad (29)$$

Equations (27), (28), and (29) can be combined to form n+1 simultaneous linear equations, whose solution provides unique values for b_i, i=0, 1, ..., n. Because the coefficient matrix for the n+1 equations is tri-diagonal, double precision numerical methods of solving for the n+1 b_i values have been found adequate for $n<50$. Given the b_i values from the solution, the n a_i values giving a minimum sum of squares can be solved from equation (24). Thus if an initial estimate for the parameter is available, the quantity SS can be minimized to find the least squares estimate of k. The value I_n is estimated by $I_n=W(t_0)-b_0$.

A second approach to solving the system of equations for the b_i could be used. A second parameter in the model can be defined as I_n, the initial compartment concentration, and can be treated as a second dimension in a nonlinear regression. With I_n given, b_0 is then defined as $W(t_0)-I_n$. The rest of the b_i can then be defined recursively from equations (27), (28), and (29). The partial derivatives with respect to the parameters could be calculated numerically.

Equations can be derived with explicit solutions for the a_i and b_i. However, these solutions require the evaluation of the exponential function with large positive quantities, i.e., exp(x) for x>100. Even though the expressions can be solved to yield analytic partial derivatives with respect to the parameter k, their use is not suited for numerical computations. Therefore the method presented above requiring the solution of a set of simultaneous equations will be used for computations.

An additional approach also will be attempted to estimate the parameter values. The parameters that minimize (Σa_i^2) (Σb_i^2) were shown to be maximum likelihood estimates. However, either the a_i's or b_i's can all be set to zero to minimize this function. Hence another method suggested is to estimate the a_i's and b_i's by the approach developed above using

$$SS = \sum_{i=1}^{n} a_i^2 + \sum_{i=0}^{n} b_i^2$$

and then solving for k by minimizing the product $(\sum_{i=1}^{n} a_i^2)$ $(\sum_{i=0}^{n} b_i^2)$.

This approach has no known statistical properties to justify its use, but offers a fourth alternative of finding parameter estimates.

Data were simulated to test the methods presented. The equation $y_i = 10000 \exp(-0.01\ t_i) + b_i$ was used to generate all sampling error data, with $t_i = 0, 4, 8, \ldots, 200$. The b_i's were normally distributed, mean zero, standard deviation 400, and were added to the function to simulate sampling error. All process variation data were simulated using the Euler method to numerically integrate the equation $dy/dt = -0.01\ y + a_i$ with a time increment of 0.1 and an initial value of $y_0 = 10{,}000$. The process was sampled at $t_i = 0, 4, 8, \ldots, 200$. The a_i's were normally distributed, mean zero, standard deviation 40, and were constant between sampling periods. Data with both process and sampling variation were simulated by first generating a set of all process variation data, and then adding a sampling error. Different a_i and b_i values were used to simulate all process variation data, all sampling variation data, and both process and sampling variation data. The FORTRAN IV code used to generate the all process variation data and both process and sampling variation data are given in White (1976:104-124).

Thirty sets of data, each with 51 observations, were simulated: (1) 10 with only sampling variation, (2) 10 with only process variation, and (3) 10 with both sampling and process variation. The data were then fitted by four different methods: (1) all sampling variation assumed, (2) all process variation assumed, (3) both sampling and process variation assumed and $\Sigma a_i^2 + \Sigma b_i^2$ minimized, and (4) both sampling and process variation assumed and $(\Sigma a_i^2)\ (\Sigma b_i^2)$ minimized.

Nonlinear least squares (Marquardt, 1963) was used to fit the simulated data for the first three methods above. The FORTRAN IV subroutines used to calculate the minimum sum of squares for each of the methods are given in White (1976:104-124). For the all sampling variation and all process variation methods, partial derivatives were calculated with analytical expressions. For both the sampling and process variation methods where the sum was minimized, derivatives were calculated by the numerical methods described by White (1976:92-95).

Parameter estimation for the fourth method above where the product $(\sum_{i=1}^{n} a_i^2)\ (\sum_{i=0}^{n} b_i^2)$ was minimized did not lend itself to solution by the Marquardt algorithm. Attempts at using the procedure failed. Therefore, another method of finding the minimum of the product was used. Hooke and Jeeves (1961) described a direct search method for finding a minimum that does not require partial derivatives of the function with respect to each of the parameters. The computer code to perform the search (White, 1976:99-103) was also used to verify the results of the Marquardt algorithm in minimizing

$$\sum_{i=1}^{n} a_i^2 + \sum_{i=0}^{n} b_i^2.$$

Results for the simulated data are presented in Table 7. The four methods do not provide very different estimates of the compartment loss coefficient k, or of the initial concentration, I_n. Some differences are noticed in the standard deviation of the mean of 10 values among the four methods, however. For data simulated with all

Table 7. Comparison of the three assumptions about random variability in estimating a compartment loss coefficient from simulated data. True parameter values are $k = 0.01$ and $I_n = 10{,}000$. Ten data sets each with 51 observations were simulated for the three combinations of theoretical variances shown. Values in the table represent the mean or standard deviation of the parameters estimated for each of the ten data sets

Method		Parameter $\hat{k}$	$\hat{I}_n$	$\hat{\sigma}_a$	$\hat{\sigma}_b$
Data simulated with $\sigma_a = 40$ and $\sigma_b = 0$					
All process variation assumed	Mean	0.01010	10,000	39.772	0.0
	Standard deviation	0.00082	0.0	2.5988	0.0
All sampling variation assumed	Mean	0.01011	10,011.0	0.0	263.07
	Standard deviation	0.00107	247.18	0.0	49.885
Both process and sampling variation assumed, sum minimized	Mean	0.01003	9,996.3	35.442	12.092
	Standard deviation	0.00089	5.588	2.322	0.8097
Both process and sampling variation assumed, product minimized	Mean	0.01008	9,996.4	35.446	12.090
	Standard deviation	0.00086	5.410	2.323	0.8092
Data simulated with $\sigma_a = 0$ and $\sigma_b = 400$					
All process variation assumed	Mean	0.01011	10,092.1	140.91	0.0
	Standard deviation	0.00071	380.61	13.967	0.0
All sampling variation assumed	Mean	0.00996	10,033.7	0.0	390.73
	Standard deviation	0.00020	110.47	0.0	20.685

Table 7. Continued.

Method		Parameter $\hat{k}$	$\hat{I}_n$	$\hat{\sigma}_a$	$\hat{\sigma}_b$
Both process and sampling variation assumed, sum minimized	Mean	0.00996	10,069.	118.94	50.356
	Standard deviation	0.00069	374.15	11.412	5.4918
Both process and sampling variation assumed, product minimized	Mean	0.00997	10,086.	118.94	50.356
	Standard deviation	0.00093	352.94	11.412	5.4918
	Data simulated with $\sigma_a = 40$ and $\sigma_b = 400$				
All process variation assumed	Mean	0.01084	9,769.6[a]	152.29	0.0
	Standard deviation	0.00257	301.77	16.598	0.0
All sampling variation assumed	Mean	0.01031	10,053.2	0.0	500.72
	Standard deviation	0.00144	381.57	0.0	50,000
Both process and sampling variation assumed, sum minimized	Mean	0.00966	10,011.3	130.04	52.821
	Standard deviation	0.00131	32.008	13.015	7.263
Both process and sampling variation assumed, product minimized	Mean	0.00952	10,011.0	130.05	52.813
	Standard deviation	0.00148	31.418	13.007	7.267

[a]The 95% confidence interval on the mean of I_n for the 10 simulations does not include the true parameter value of 10,000, i.e.

$[9{,}769.6 + t(0.05) * 301.77 / \sqrt{10}\ ] < 10{,}000.$

process variation, the standard deviation of I_n for the methods that assume both types of variation is much smaller than the all sampling variation method. The all process variation method has a standard deviation for I_n of 0.0 because the compartment is observed exactly at t=0, and hence I_n was always estimated as 10,000 for this method. Note that only the all process variation method provides a reliable estimate of the process variance, σ_a. The all process variation method does not seem to give better estimates of the parameters k and I_n, however.

For data simulated with all sampling error, the all sampling error method provided the best estimates. The standard deviations for the means of $\hat{k}$ and $\hat{I}_n$ were smaller than any of the other methods. Also the sampling error variance, σ_b, was estimated with little bias. For data simulated with both sampling and process variation, all four methods provided close estimates of the parameters k and I_n. However none provided good estimates of the process and sampling standard deviations, σ_a and σ_b.

Minimization of (Σa_i^2) (Σb_i^2) did not seem to appreciably change the estimates of k, I_n, σ_a, and σ_b from those of the summation method. These two methods appear to provide unbiased estimates of k and I_n, but not of σ_a and σ_b. The two maximum likelihood methods provided good estimates of σ_a and σ_b in the cases where the model fitted the data. The only case where the 95% confidence interval on the mean of k or I_n for the 10 simulations did not include the true value was for I_n on data simulated with $\sigma_a = 40$ and $\sigma_b = 400$, where the all process

variation method was used. However this method estimates I_n as the observed value at t = 0. In this instance, the simulated data actually differed from the expected value.

In summary, when the true model is known to be a single compartment constant loss coefficient model, any of the four methods used will provide good estimates of the parameters k and I_n. However, only in two cases, i.e., all process variation and all sampling variation, will any of the methods correctly estimate the variance.

All four methods also were used to estimate the loss rate coefficient for the marsh water (Table 8). The all sampling error estimate of k was different from the previous value given in water-sediment model I because an additional observation at t=0 was included. The initial concentration of HTO in the marsh is measured exactly if all the error is assumed to be process error, and hence I_n is not estimated, but observed. The methods which assumed both sampling and process variation provide much more realistic estimates of I_n than the all sampling variation method. A poor fit was apparent at the initial times of the all sampling variation method in Fig. 1.

Because the observed values of the water compartment were means of from 4 to 149 samples, the sampling error can be estimated from the raw data. The mean square for pure error, that is, the combined mean squared error around the means of the observations at each time (Draper and Smith, 1966:26) was approximately 4,500. Some arbitrary decisions were made in this calculation, because initially HTO was not spread uniformly through the area. However, the value compares favorably to the estimated sampling error variance of approximately

Table 8. Comparison of four methods for estimating a compartment loss coefficient from the marsh water.

Method	$\hat{k}$	$\hat{I}_n$	$\hat{\sigma}_b$	$\hat{\sigma}_a$	$\hat{\sigma}_a + \hat{\sigma}_b$
All sampling variation assumed	0.0114	2612.	35286.	0.	35286.
All process variation assumed	0.0416	3565.	0.	16922.	16922.
Both process and sampling variation assumed, sum minimized	0.0327	3289.	3233.	2442.	5675.
Both process and sampling variation assumed, product minimized	0.0318	3287.	3247.	2430.	5677.

3,240 from the both sampling and process variation methods, although this value was shown to be biased by the simulation results.

Analysis of the a_i vector from the methods that assumed both sampling and process variation was helpful in assessing the fit of the model to the observed data. For the particular case analysed, the last 40 a_i values were positive. This indicated the single compartment, constant coefficient model provided a poor representation of HTO loss from the marsh water. This was the case, since the HTO loss from the marsh was complicated by the initial uptake of HTO by the

sediment, and subsequent release as the water compartment changes to reverse the flow gradient. Hence, a single compartment constant loss coefficient model will not be realistic for this system. The differences between the all sampling error estimates of k and I_n and those of the both sampling and process variation methods probably resulted from the lack of fit of the model. This discrepancy in estimates was not noticed with simulated data (Table 7) where the model was known to be correct.

Multiple Compartments

The methods described for the single compartment case can be extended to an m compartment case. Consider the m differential equations in matrix notation

$$X'(t_i) = KX(t_i) + E(t_i) \tag{30}$$

where $X'(t_i)$ is the rate of change of the vector $X(t_i)$ at time t_i, K is the coefficient matrix, and $E(t_i)$ is the vector of process errors at time t_i. The error vector is of the same form as for the one compartment case:

$$E(t_i) = A_i \ [U(t-t_{i-1}) - U(t-t_i)]$$

where A_i is a vector of normally distributed process errors with mean zero and variance vector σ_a^2. The solution to equation (30) is known to be (Hirsch and Smale, 1974) of the form

$$X(t_i) = \exp(t_i K) \ F(t_i)$$

Solving for the vector $F(t_i)$ leads to the solution

$$X(t_i) = \exp(-_iK) \{ \sum_{j=1}^{i} - [\exp(-t_iK) - \exp(-t_{j-1}K)] K^{-1}A_j + X(t_0)\} \quad (31)$$

Since values of $X(t_i)$ are only observed in conjunction with sampling error, the associated sampling error vector, B_i, $N(0, \sigma_b^2)$, must be added to the solution:

$$Y(t_i) = \exp(t_iK) \{ \sum_{j=1}^{i} (-[\exp(-t_jK) - \exp(-t_{j-1}K)] K^{-1}A_j) + X(t_0)\} + B_i \quad (32)$$

The previous value of Y, $Y(t_{i-1})$ and the associated sampling error B_{i-1} can be substituted into equation (32) to produce a simpler form

$$Y(t_i) - B_i = \exp((t_i-t_{i-1}) K) \{Y(t_{i-1}) - B_{i-1} + [I-\exp(-(t_i-t_{i-1}) K)] K^{-1}A_i\} \quad (33)$$

where I is the identity matrix of dimension m. Note that $(I-\exp((t_i-t_{i-1})K))$ commutes with K^{-1} since $\exp((t_i-t_{i-1})K)K^{-1}$ commutes. This is known because

$$\exp((t_i-t_{i-1})K) = I + \sum_{j=1}^{\infty} \frac{(t_i-t_{i-1})^j K^j}{j\,!}$$

with which it is easily seen that K^{-1} commutes. Equation (33) can be rearranged to solve for A_i in terms of B_i

$$A_i = -K\,[I-\exp((t_i-t_{i-1})K)]^{-1}\ \{Y(t_i)-B_i - \exp((t_i-t_{i-1})\,K)\ (Y(t_{i-1}) - B_{i-1})\} \tag{34}$$

Using the same technique as applied to the single compartment case minimizes the sum of squares for the B_i and A_i. Hence

$$SS = \sum_{i=0}^{n} B_i{}^T B_i + \sum_{i=1}^{n} A_i{}^T A_i \tag{35}$$

Equation (34) can be substituted into equation (35) and then differentiated with respect to B_i, i=0, ..., n to produce a set of simultaneous equations in B_i. These equations can be solved for the B_i's and then equation (34) can be used to obtain the A_i's.

The procedure is cumbersome because the simultaneous equations for B_i cannot be solved if n x m is much greater than 50. For small m and few observations, however, the method is workable. Thus least squares estimates of the coefficient matrix K can be obtained if both process and sampling variation are assumed.

Two Compartment Crayfish Model

A variation of the m compartment method was used to estimate the parameters of the organism model. First the values of the process and sampling errors, a_i and b_i, for the water compartment were calculated.

The organism was assumed not to affect the water compartment so that the water compartment errors should be calculated separately from the organism observations. Then, the marsh water was assumed to be a forcing function on the organism model, and a two compartment model was written

$$X'(t_i) = KX(t_i) + E(t_i) + bZ(t_i) \tag{36}$$

where $X(t_i)$ is a two-component vector of the unbound and bound compartments. $Z(t_i)$ is a two component vector; the first element is the water concentration, W, at time t_i (see equation (21)), and the second element is zero, since no input from the marsh water to the bound compartment was assumed. Parameter b is the transfer coefficient from the marsh water to the unbound compartment, and is equivalent to b in the all sampling error representation of the organism model. $E(t_i)$ is the autocorrelated process error.

Equation (36) was solved by the same method as described for the m compartment case. The vector $F(t_i)$ was somewhat more complicated due to the forcing function, $Z(t_i)$. The solution with sampling error is

$$X(t_i) = \exp(t_iK)\{ \sum_{j=1}^{i} - [\exp(-t_jK) - \exp(-t_{j-1}K)]K^{-1} A_j$$

$$+ X(t_0) - B_0 + b \int_0^{t_i} \exp(-sK)\, Z(s)\, ds\} + B_i \tag{37}$$

The solution is simplified by replacing the summation with an expression from the previously observed value:

$$X(t_i) = \exp((t_i - t_{i-1})K) \quad \{X(t_{i-1}) - B_{i-1}$$

$$+ \quad [I - \exp(-(t_i - t_{i-1})K)]\ K^{-1}\ A_i\}$$

$$+ \exp(t_i K) \int_{t_{i-1}}^{t_i} \exp(-sK) \quad Z(s)\ ds \ + \ B_i \qquad (38)$$

The integral in equation (38) can be solved to provide an explicit expression. Let Q be the eigenvector matrix, and D the diagonal matrix of eigenvalues such that

$$K = Q\ D\ Q^{-1}$$

Also let Q have values

$$Q = \begin{bmatrix} q_{11} & q_{12} \\ q_{21} & q_{22} \end{bmatrix}$$

and D have values

$$D = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

Then

$$\exp(t_i K) \int_{t_{i-1}}^{t_i} \exp(-sK) \quad Z(s)\ ds$$

$$= \frac{b}{q_{11}q_{22} - q_{12}q_{21}} \quad (I_n + \frac{1}{k} \quad \sum_{j=1}^{\ell} \quad (\exp(t_j^* k)$$

$$- \exp\ (t_{j-1}^* K)\ a_j)\ Q\ U \qquad (39)$$

where U is the vector

$$\begin{bmatrix} \frac{-q_{22}}{\lambda_1+k} \left[\exp(-t_i k) - \exp((t_i-t_{i-1})\lambda_1 - t_{i-1}\, k)\right] \\ \frac{q_{21}}{\lambda_2+k} \left[\exp(-t_i k) - \exp((t_i-t_{i-1})\lambda_2 - t_{i-1}\, k)\right] \end{bmatrix}$$

I_n is the initial concentration of the marsh water compartment and is identical to the I_n of equation (21). The small k is the water compartment loss coefficient, also from equation (21). The summation in equation (39) is over the range $j = 1, \ldots, \ell$. It is not necessary that the crayfish observations be taken at the same time that the water compartment was observed. Water compartment observation times are denoted by t_i^*. The time t_ℓ^* is the smallest time at which the water compartment is observed such that $t_\ell^* \geq t_i$. The above integration involves representing the matrix exponential in the form $Q \exp(tD)\, Q^{-1}$. The integration was then performed element by element after the matrices were multiplied.

The method for finding expressions for B_i and A_i was the same as for the m compartment system. Substituting for the A_i's in the expression

$$SS = \sum_{i=0}^{n} B_i^T B_i + \sum_{i=1}^{n} A_i^T A_i \qquad (40)$$

and differentiating with respect to B_i a system of simultaneous equations was formed. These were solved to find values for each of the B_i vectors (i = 0, ..., n). Then the values were replaced in equation (38) to solve for the A_i vectors (i = 1, ..., n). Details are given in White (1976:125-127).

The sum of squares in equation (40) was minimized to form the least squares estimates of the coefficient matrix K and the transfer coefficient b. An unsuccessful attempt was made to find the parameter estimates for the crayfish data. A program was written in SPEAKEZ (Cohen et al., 1974) to solve the set of 56 simultaneous equations (28 observations of 2 compartments). Writing the program in SPEAKEZ provided an easily written, quickly debugged program, albeit an expensive program to execute in terms of computer time. The version of Marquardt's nonlinear least squares method was used to minimize the sums of squares, SS. The partial derivatives with respect to each of the parameters were solved numerically. The program required the value of the residual to be returned for each observation. The value returned was calculated as $\sqrt{b_i^2 + a_i^2}$, $i = 0, 1, \ldots, n$, where $a_0 = 0$. The program was not allowed to converge because of the extreme amount of computer time required. Parameter values that are thought to be fairly close to the least squares estimates are given in Table 9. No doubt a more efficient program could be written in a lower level language to decrease the amount of computer time required for estimating the parameters. Until more is known of the properties of the estimates from the method described for a single compartment, an efficient program is not required. Once the estimators are shown to have the desired properties, a much more efficient program can be developed.

The parameter estimates in which both sampling and process errors are assumed (Table 9) differ considerably from estimates in which only

Table 9. Approximate values of crayfish model parameters estimated assuming both process and sampling errors. Notation follows Fig. 16.

Parameter	Approximate least squares estimate
Transfer coefficient from water to unbound, b	34.713
Unbound loss coefficient, c	26.279
Bound to unbound transfer coefficient, d	113.86
Unbound to bound transfer coefficient, f	0.15436
Bound loss coefficient, g	-113.01

sampling error is assumed (Table 6). However, the main conclusion made from the values, i.e., the majority of the bound tritium comes from food, does not change. The water to unbound compartment transfer coefficient, b, appears to show the greatest difference. This difference probably only reflects the different model parameters for the water compartment, however, since the water model parameters also were estimated with a method that assumed both process and sampling errors for the results reported in Table 9. The different water model may explain much of the change in values. A thorough analysis cannot be made since the values reported in Table 9 are only approximate.

SUMMARY

A simulation model of tritium kinetics was developed from data collected in a Lake Erie marsh. Approximately 11 Curies of tritiated water (HTO) were released into the marsh, and loss of HTO was monitored for one year. Models were fitted to these data with nonlinear least squares to provide maximum likelihood estimates of parameters.

The first model of the physical components of the marsh ecosystem ignored environmental variation and provided an unsatisfactory fit to the observed data. However the loss rate coefficient for the marsh water, based on a year's data, showed excellent agreement with a study conducted in Georgia.

In a second model of the marsh water and sediment system, the loss of HTO from the marsh was a function of seasonal variation. Particularly important in this model was the marsh water temperature, since the equilibrium vapor pressure of HTO in the atmosphere was determined by the water temperature. A simulation in which the marsh water was warmed during the winter showed a faster rate of loss of HTO from the marsh than when the water temperature was not raised. The model also provided a good prediction of the HTO concentration in the marsh water for a previous study conducted at the same marsh site. Since this study took place during the period from July to November, whereas the parameters for the model were estimated from data primarily collected during fall and winter, the good predictions provided added evidence that the model has predictive capability for varying environmental

regimes. HTO is also assumed to move into the sediment, which provides for a more realistic model than has been presented previously.

The model for tritium in an organism was developed with the assumption of constant kinetic coefficients. Analytic solutions were then available. The model allowed the exchange of tritium between the body water and tissue compartments. This was a more realistic assumption about tritium kinetics in an organism than was implicit in previous models developed by other investigators. The model was fitted to data on crayfish to obtain maximum likelihood estimates of parameters. The majority of the tissue bound tritium appeared to come from food for this species.

A method of estimating parameters for compartment systems was developed. The method assumed both process variation and sampling variation, which was a much more realistic assumption than assuming either type of error was the only one present. If process and sampling errors are all independent and mean zero and have constant variances σ_a^2 and σ_b^2, respectively, then the parameter estimates developed are least squares estimates. Maximum likelihood estimators are only obtained when either $\sigma_a^2 = 0$ or $\sigma_b^2 = 0$. For simulated data, methods that assumed both process and sampling error did not improve parameter estimates over methods that assumed only process variation or only sampling variation. However, for data on the marsh water compartment, widely different parameter estimates were obtained from the different methods. These differences in parameter estimates probably indicated

that the model being fitted was not a good representation of the underlying process.

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